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THE TRANSPORT OF HEAVY METALS BY THE MISSISSIPPI RIVER AND THEIR FATE IN THE GULF OF MEXICO

A Dissertation

by

JOHN HAROLD TREFRY III

Submitted to the Graduate College of
Texas A&M University
in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

May 1977

Major Subject: Oceanography

THE TRANSPORT OF HEAVY METALS BY THE MISSISSIPPI RIVER AND THEIR FATE IN THE GULF OF MEXICO

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ABSTRACT

The Transport of Heavy Metals by the Mississippi River and their Fate in the Gulf of Mexico (May 1977)

John Harold Trefry III, A.B., Syracuse University; M.S., Texas A&M University

Chairman of Advisory Committee: Dr. B. J. Presley

Significant differences in total and leachable concentrations of some metals were observed between Mississippi River suspended matter and Gulf of Mexico sediments. These variations are related to diversity in Gulf sediment redox conditions, accumulation rates and grain-size distribution.

Suspended particulates transport >90% of the Mississippi River metal load. Hydrous oxides and aluminosilicate lattices are the primary phases of particulate metal transport. In general, total and leachable metal concentrations in river suspended matter are seasonally and spatially uniform. During low river flow, an eight-fold increase in the organic content of the suspended matter brought about a decrease in particulate Fe and Al values and a marked increase in Mn, Zn, Cu and Cd concentrations. Average SiO_2, Al_2O_3 and K_2O concentrations in Mississippi River particulates are similar to crustal abundances. Particulate Na_2O, CaO and MgO values are 60-80% below crustal levels; however a high river dissolved load of these elements offsets the low particulate levels. No significant change in the total or leachable heavy metal concentrations of river suspended matter was found across the freshwater-seawater interface.

Mississippi Delta sediments have 20-40% lower Mn, Cu, Co, Ni and Zn

concentrations and metal/Al ratios than river particulates which is the direct result of a decrease in oxide-phase metal content. Iron, Cr, V and Al concentrations and grain-size distribution in suspended matter and sediments are similar. Lead and Cd concentrations in delta sediments are 70 and 200% respectively above natural levels. The onset of this Pb and Cd pollutant input is traced to the late 1800's.

Reducing conditions in delta sediments induce a loss of oxide-phase Mn, Fe and perhaps other metals via reduction-diffusion. Interstitial water Mn gradients, in particular, support such a mechanism. Calculated fluxes of dissolved Mn from the sediments to the overlying seawater range from 200 to >1000 μg Mn cm^{-2} y^{-1}. This process occurs over at least 1000 km of the delta where sedimentation rates are >0.5 g cm^{-2} y^{-1} as determined by Pb-210 dating (SHOKES, 1976). Gulf of Mexico outer shelf and slope sediments which accumulate at <0.5 g cm^{-2} y^{-1} are characterized by surficial Mn-rich zones (2000-8000 μg Mn/g) and complementary interstitial Mn profiles.

Manganese, Cu, Co and Ni concentrations are high in deep Gulf sediments relative to river particulates. Observed metal enrichment is most striking in the strictly pelagic Sigsbee Knoll sediment where Cu, Co and Ni concentrations (ratioed to Al) are ∿50% above river particulate levels and Mn concentrations are almost triple river values. Little change in average Fe, Zn, Pb, Cr, and V concentrations occurs between nearshore and abyssal environments.

Evidence of post-depositional remobilization of Mn, and to a lesser degree Ni, Fe, Cu and Co, is found throughout the deep Gulf. For example, surface layers of 1.5% Mn show up in slope cores. In abyssal areas, metal maxima are found at depth as a relict of past environmental conditions.

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INTRODUCTION

Background and Statement of Purpose

River particulates dominate metal input from the continents to the oceans. The bulk of this flux is deposited in rapidly accumulating nearshore sediments. The quantitative importance of river particulates and nearshore sediments to the geochemical cycling of metals is supported by the mass balance calculations summarized in Table 1. Particulate and dissolved metal species not removed in coastal areas migrate to the deep sea. There, slow processes promote the observed metal enrichment of sediments and ferromanganese nodules. Although much is known about metal distribution, partitioning and accumulation rates in pelagic sediments and nodules, there is a paucity of similar information about river particulates and nearshore sediments. This study is designed to increase our understanding of riverine metal fluxes and the chemical changes which occur when metals are transported to the marine environment and deposited in areas of varying sedimentation rate, grain-size distribution and redox conditions.

Observed enrichment of many trace metals in pelagic sediments and ferromanganese nodules relative to continental crust has induced numerous studies and hypotheses over the past several decades (CLARKE, 1924; CORRENS, 1937; REVELLE, 1944; PETTERSSON

Format from Geochimica et Cosmochimica Acta.

Table 1. Geochemical mass balance of heavy metals in seawater (all fluxes in g/y).*

Metal	River Input Dissolved	River Input Particulate	Others**	TOTAL Input	Nearshore sediments	Deep Sea Clay	Deep Sea Carbonate	Manganese Nodules	TOTAL Output
Fe	$<0.01 \times 10^{14}$	8.64×10^{14}	0.55×10^{14}	9.19×10^{14}	8.18×10^{14}	0.60×10^{14}	0.03×10^{14}	0.02×10^{14}	8.83×10^{14}
Mn	0.02×10^{13}	1.74×10^{13}	0.60×10^{13}	2.36×10^{13}	1.48×10^{13}	0.62×10^{13}	0.01×10^{13}	0.16×10^{13}	2.27×10^{13}
Zn	0.32×10^{12}	1.28×10^{12}	0.16×10^{12}	1.76×10^{12}	1.62×10^{12}	0.15×10^{12}	0.04×10^{12}	0.01×10^{12}	1.82×10^{12}
Cu	0.06×10^{12}	1.01×10^{12}	0.15×10^{12}	1.22×10^{12}	0.84×10^{12}	0.23×10^{12}	0.03×10^{12}	0.03×10^{12}	1.13×10^{12}
Ni	0.01×10^{12}	1.37×10^{12}	0.11×10^{12}	1.49×10^{12}	0.96×10^{12}	0.23×10^{12}	0.04×10^{12}	0.05×10^{12}	1.26×10^{12}
Pb	0.32×10^{11}	3.66×10^{11}	0.31×10^{11}	4.29×10^{11}	2.78×10^{11}	0.74×10^{11}	0.20×10^{11}	0.09×10^{11}	3.81×10^{11}
Cr	0.03×10^{12}	1.83×10^{12}	0.24×10^{12}	2.10×10^{12}	1.74×10^{12}	0.08×10^{12}	0.02×10^{12}	$<0.01 \times 10^{12}$	1.84×10^{12}
Co	0.06×10^{11}	3.66×10^{11}	0.46×10^{11}	4.18×10^{11}	2.61×10^{11}	0.68×10^{11}	0.12×10^{11}	0.30×10^{11}	3.71×10^{11}
V	0.03×10^{12}	2.47×10^{12}	0.36×10^{12}	2.86×10^{12}	2.26×10^{12}	0.11×10^{12}	0.02×10^{12}	0.01×10^{12}	2.40×10^{12}

*See Appendix A for calculation details.

** Glacial flour, marine erosion, atmospheric dust flux, and subsurface input.

and ROTSCHI, 1952; YOUNG, 1954; GOLDBERG and ARRHENIUS, 1958; WEDEPOHL, 1960; EL WAKEEL and RILEY, 1961; CHOW and PATTERSON, 1962; LANDERGREN, 1964; TUREKIAN and SCHUTZ, 1965; BOSTRÖM and PETERSON, 1966; CHESTER and HUGHES, 1966, 1969; PRICE and CALVERT, 1970; BENDER et al., 1971; DYMOND et al., 1973; CHESTER et al., 1976 to mention a few). The necessary supply of metals to account for deep-sea enrichment has been attributed to continental runoff, volcanic and hydrothermal input, post-depositional migration, biological mediation and cosmic flux. The present consensus is that trace metal enrichment of pelagic sediments is indirectly related to sedimentation rate and that, except for "metalliferous" mid-ocean ridge areas, the metals are derived primarily from the continents.

Despite the importance of the continental metal flux, only a small body of literature considers metal concentrations or fluxes to the ocean by continental detritus (TUREKIAN and SCOTT, 1967; WINDOM et al., 1971; PERHAC, 1972; GIBBS, 1973; CARPENTER et al., 1975; and MARTIN and MEYBECK in CHESTER and ASTON, 1976). Furthermore, large variations in river particulate metal concentrations are commonly reported and may result from localized pollution and mineral sources and from sample contamination. For example, TUREKIAN and SCOTT (1967) found order-of-magnitude differences in Cr, Ag, Mo, Ni, Co and Mn concentrations of particulates from 18 U.S. and 2 foreign rivers and noted that western U.S. rivers and the Rhone (France) had metal concentrations which approach crustal averages whereas eastern U.S. rivers and Rio Maipo

(Chile) had significantly higher levels. Recent unpublished data of MARTIN and MEYBECK (in CHESTER and ASTON, 1976) show that particulate Fe, Al, Mn, Ni, Co, Cr and V concentrations in several large rivers (Amazon, Congo, Ganges, Mekong and Orinoco) approximate crustal abundance values whereas Cu, Pb and Zn concentrations were generally much higher. CARPENTER et al. (1975) found order-of-magnitude variations in Susquehanna River particulate metal concentrations on a seasonal basis and point out the importance of an integrated program in order to obtain reliable flux data. Flux calculations are further hampered by generally inadequate knowledge of river suspended loads. Only one investigator (GIBBS, 1973) has ever analyzed the different phases by which river particulate metals may be transported.

Although river metal loads are generally not well characterized, there has been a considerable effort to understand the physico-chemical interactions which are believed to occur across the freshwater-seawater interface (LOWMAN et al., 1966; KHARKAR et al., 1968; COONLEY et al., 1971; EVANS and CUTSHALL, 1973; WINDOM, 1975; BOYLE et al., 1974). Unfortunately, the results are somewhat conflicting as to whether desorption, adsorption or other phenomena occur. This conflict is not surprising in view of the numerous variables such as dissolved species concentrations, pH, temperature, equilibration time, freshwater-seawater mixing properties, and mineralogy and concentration of suspended matter which may influence metal behavior (MURRAY and MURRAY, 1973; BOYLE et al., 1974; O'CONNOR and KESTER, 1975; PARKS, 1975).

Because the dissolved fraction should provide the most sensitive indicator of metal uptake or release, it has been most studied. There is no clear reference to a study of changes in particulate metal concentrations across the freshwater-seawater mixing zone, even though such changes may give a rough estimate of the quantitative importance of sorption to the overall riverine metal flux.

Nearshore sediments are the major sink for the continentally derived metals (Table 1). These sediments comprise a highly variable environment which includes estuaries, bays, deltas and continental shelves and are made-up of clay-rich muds, pure sands, biogenous oozes and rapidly accumulating phosphorite and ferromanganese nodules. It follows that reported nearshore sediment metal concentrations are similarly variable (HIRST, 1962; MOORE, 1963; CALVERT and PRICE, 1970; HOLMES, 1973; and BRULAND et al., 1974), making it difficult to quote any representative values. WEDEPOHL'S (1960) metal averages for nearshore sediment approximate crustal abundance data and are probably reasonable for the majority of cases. Although there has been a recent increase in the amount of nearshore sediment metal data, little of this work has focused on metal accumulation rates, metal partitioning or diagenetic alterations involving metals.

Available data (BRULAND et al., 1974; and CALVERT, 1976) show that nearshore sediments accumulate trace metals on the order of 1-10 $\mu g\ cm^{-2}y^{-1}$ or about 10-100 times faster than in pelagic sediments. But, nearshore sedimentation rates are 100-1000 times faster than those in the deep sea and thus the net result is that

some metals are in higher concentrations in pelagic sediments than in nearshore sediments. CHOW and PATTERSON (1962) explain the above pattern by showing that the rate of chemical deposition of Pb is uniform throughout the ocean and that variations in the mechanical deposition rate (i.e. sedimentation rate) account for differing sediment Pb concentrations (Table 2). In order for the average chemical

Table 2. Mechanical and chemical accumulation rates of Pb in pelagic sediments (from CHOW and PATTERSON, 1962)

Sediment type	Sedimentation rate ($g\ cm^{-2}10^{-3}y^{-1}$)	Mechan. deposited Pb ($\mu g/g$)	Chem. deposited Pb ($\mu g/g$)	Accum. rate Mechan. Pb ($\mu g\ cm^{-2}10^{-3}y^{-1}$)	Accum. rate Chem. Pb ($\mu g\ cm^{-2}10^{-3}y^{-1}$)
Rapidly depositing oozes	0.43	9	14	3.9	6.0
Moderate (light sediments)	0.10	14	28	1.4	2.8
Slow (dark clays)	0.027	14	74	0.4	2.0
Very slow (Mn nodules)	0.0088	(1)	970	0.009	8.5
					$\bar{x} = 4.7$

deposition rate of $\sim 5\mu g$ Pb $cm^{-2}10^{-3}y^{-1}$ (Table 2) to measurably change sediment Pb concentrations, sedimentation rates must be $<2g\ cm^{-2}10^{-3}y^{-1}$. This is certainly not the case in nearshore sediments and thus any chemical deposition of Pb in the nearshore environment would be completely obscured. BENDER et al. (1971) also find total Mn accumulation rates to be relatively uniform over the world ocean ($1.3mg$ Mn $cm^{-2}10^{-3}y^{-1}$) except on active ridges (eg. East Pacific Rise, $35mg$ Mn $cm^{-2}10^{-3}y^{-1}$). Assuming a large percentage of this Mn to be chemically deposited, no increase in sediment Mn concentrations via chemical deposition would be observed until sedimentation rates were $<50g\ cm^{-2}10^{-3}y^{-1}$. Time is thus a key factor in considering metal enrichment of pelagic sediments, however, other factors must

be examined to find chemical changes involving metals in nearshore sediments.

A more likely possibility is that after deposition in anoxic sediments or subsequent exposure to reducing conditions, metals may be remobilized and released to the interstitial water. When the entire sediment column is anoxic there may be a flux of solubilized species to the overlying seawater. When anoxic sediment is overlain by oxic sediment, metals may dissolve at depth, diffuse upward, reoxidize in the surface oxic layer and thus greatly concentrate a given species over natural levels. Likewise, metals rendered more soluble by oxidizing conditions may be released from sediments where there is a surface oxic zone.

Remobilization of Mn under reducing conditions, for example, is quite dramatic and well documented (LYNN and BONATTI, 1965; PRESLEY et al., 1967; LI et al., 1969; CALVERT and PRICE, 1972; ROBBINS and CALLENDER, 1975; HOLDREN et al., 1975). A hypothetical reaction for the reduction of Mn may be written as:

$$CH_2O + 2MnO_2 + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O \qquad (1)$$

with the amount of available organic matter and the sedimentation rate controlling the extent to which this reaction occurs.

Fig. 1 summarizes observed dissolved Mn profiles in seawater and interstitial water. Case I is observed where a stratified water column with anoxic bottom water is found (eg. the Black Sea, SPENCER and BREWER, 1971). Under these conditions, Mn is reduced and concentrated in the water column. When oxic waters overlie anoxic sediment (Case II), maximum metal remobilization occurs at

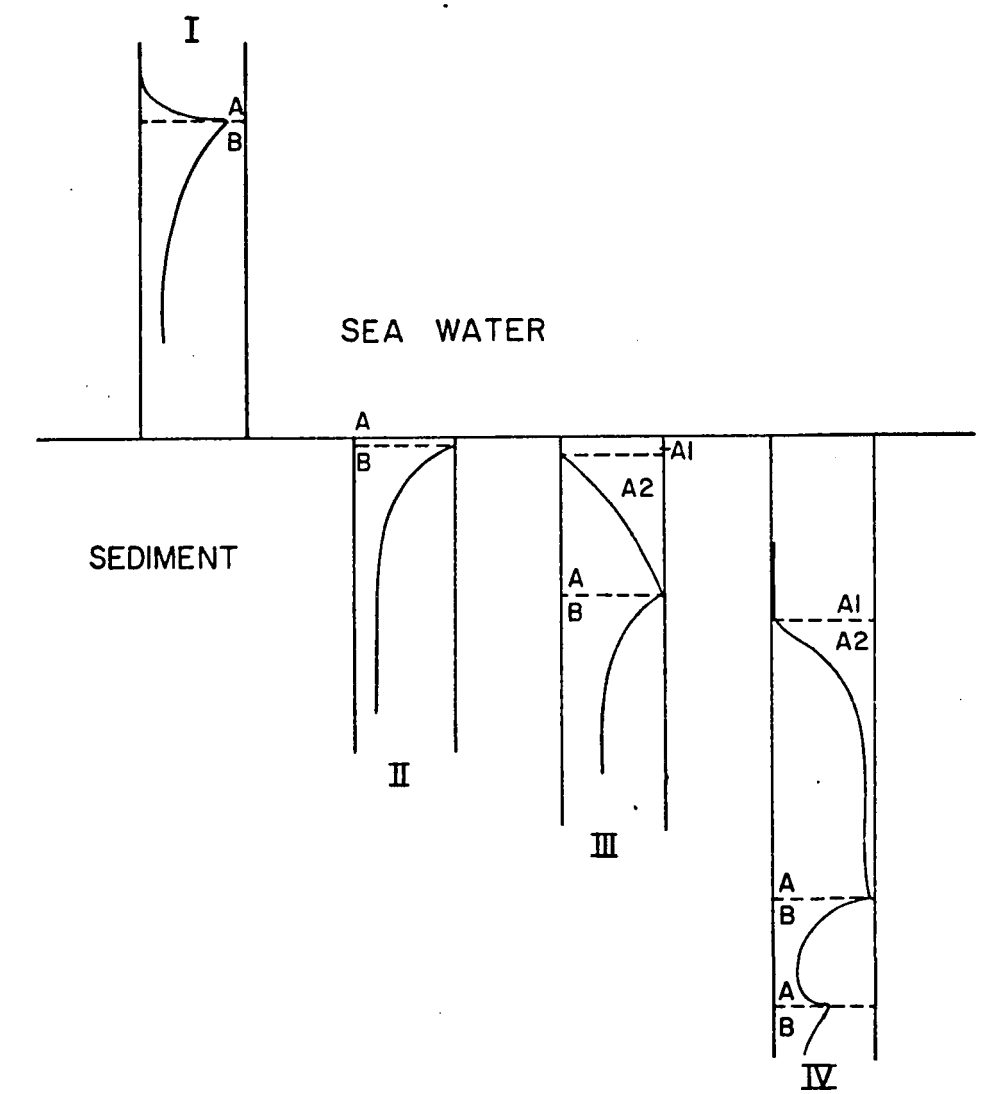


Fig. 1. Seawater-interstitial water dissolved Mn profiles as a function of the anoxic-oxic boundary (A-B in Cases I and II; A1-A2 in Case III; and A1-A2 and A-B in Case IV) and the region of maximum Mn remobilization (A-B), (from ELDERFIELD, 1976).

the sediment-water interface or in the top millimeters of sediment. Any net diffusive flux from the sediment is a function of the depth of the oxidized layer. In Case III, mildly reducing conditions allow a well-defined oxic zone (A-1) to develop wherein remobilized metals may be trapped and greatly concentrated over natural levels. ROBBINS and CALLENDER (1975) showed that the negative interstitial Mn gradient observed below the A-B boundary (Fig. 1, Cases II and III) may be controlled by precipitation of rhodochrosite ($MnCO_3$). Finally, Case IV exemplifies a possible pattern for slowly accumulating deep-sea sediment when there is a thick oxidized zone wherein there may be discrete anoxic segments.

Cases II and III (Fig. 1) are most often cited in the literature (LI et al., 1969; CALVERT and PRICE, 1972; ROBBINS and CALLENDER, 1975; HOLDREN et al., 1975), and certainly both of these qualitative models are applicable to the Mississippi Delta. However, most previous work has focused on balancing the upward diffusive flux of interstitial Mn with the accumulation of "excess" manganese in surface sediments. It has generally been assumed that net Mn losses from the sediment column are minimal. The diffusive flux of dissolved species is estimated by:

$$F = - D_s \frac{dc}{dx} + wc \qquad (2)$$

where D_s = diffusion coefficient, corrected for porosity and tortuosity (cm^2/y)

c = concentrations of dissolved species ($moles/cm^3$)

dx = thickness of sediment from depth of maximum remobilization to the sediment-seawater interface (cm)

w = sedimentation rate (cm/y).

Such fluxes may greatly alter and redistribute metals in continental shelf and slope sediments. The magnitude of diffusive fluxes for Mn may be on the order of mg $cm^{-2}y^{-1}$ (ELDERFIELD, 1976).

As previously mentioned, most reported sediment metal values are for total concentration and do not consider the various phases in which metals may be found. Soil chemists, on the other hand, have used chemical leaching techniques for many years and these efforts have been carried over to marine sediment work. GOLDBERG and ARRHENIUS (1958) used EDTA to remove "readily soluble phases" and HIRST and NICHOLS (1958) leached with acetic acid to remove the "non-detrital" sediment metal fraction. CHESTER and HUGHES (1967, 1969) used the reducing agent hydroxylamine hydrochloride and acetic acid sequentially to chemically remove metal oxides and discern the sediment "hydrogenous" metals from the "lithogenous" metals. PRESLEY et al. (1972) sequentially leached Saanich Inlet sediments with acetic acid-hydroxylamine hydrochloride (reducible fraction), peroxide (oxidizable fraction) and $HF-HNO_3-HClO_4$ (residual fraction). GIBBS (1973) similarly used $MgCl_2$, citrate buffered $Na_2S_2O_4$ and NaOCl to separate exchangeable, oxide, and organically bound metals from lattice-held species of river suspended matter. The overall results of chemical partitioning of sediment metals have allowed quantification of the oxide phase metals which are removable in various strength reducing agents, the lattice-held metals and to some degree the organic and sulfide bound metals.

These techniques, when applied to pelagic sediments (CHESTER

and coworkers, 1967, 1969, 1970, 1976), have shown that certain elements which are enriched in deep-sea sediments (Mn, Cu, Ni, Co, Zn) have a high "non-lattice" (or hydrogenous) component whereas metals such as V and Cr which are not enriched have a negligible non-lattice fraction. This emphasizes the importance of hydrogenous phases but does not completely define their source. Similar techniques also need to be applied to river particulates and nearshore sediments.

The overall purpose of this research was to increase our understanding of the marine geochemical cycling of heavy metals. To do so, the study sought to quantify and characterize the metal load of the Mississippi River and to identify chemical alterations and reactions which occur when metals are removed to Gulf of Mexico sediments in areas of varying sedimentation rate, grain-size distribution and redox conditions. The specific objectives were: (1) to determine the present-day rates of addition of dissolved and particulate metals to the Gulf of Mexico from the Mississippi River, (2) to isolate the chemical phases of particulate metal transport by the river and determine whether river particulates typify average crustal material, (3) to identify alterations in metal distribution in river particulates across the freshwater-seawater interface, (4) to determine metal concentrations and accumulation rates in nearshore sediments (Mississippi Delta) and the extent of metal remobilization within these sediments, and (5) to identify any trace metal enrichment in Gulf of Mexico pelagic sediment and relate it to grain size, Al, $CaCO_3$,

sedimentation rate and other determinants of metal concentration. The Mississippi River distributive province is a particularly good place to accomplish the above objectives. In this one region the geochemistry of continental detritus from a single source (with no hydrothermal or volcanic complications) may be compared with that of resulting sediments in varied depositional environments.

Study Area: Mississippi Delta - Gulf of Mexico

The Mississippi River drainage basin stretches from New York to Montana and from Canada to the Gulf of Mexico (Fig. 2) and includes 41% of the conterminous United States. The river transports annually 5.7×10^{14}ℓ of water (ISERI and LANGBEIN, 1974), 2.8×10^{14}g of suspended sediment (U.S. ARMY CORPS OF ENGINEERS, 1950-1974) and 1.4×10^{14}g of dissolved solids (LEIFESTE, 1974). These averages may vary substantially on both an annual and a seasonal basis. The total sediment load of the river has decreased notably since the early 1950's as a result of upstream construction of dams and farm ponds. The seasonal water flow regime, however, remains constant with a three month low flow (September-November) followed by a slow rise, flood crest and gradual falling over the remaining months.

The Mississippi River sediment load accounts for about two-thirds of the total sediment delivered to the Gulf of Mexico. Mississippi River sediment is deposited over an area at least as large as that outlined in Fig. 3. This region, including the lower Mississippi River, is the setting for the present study.

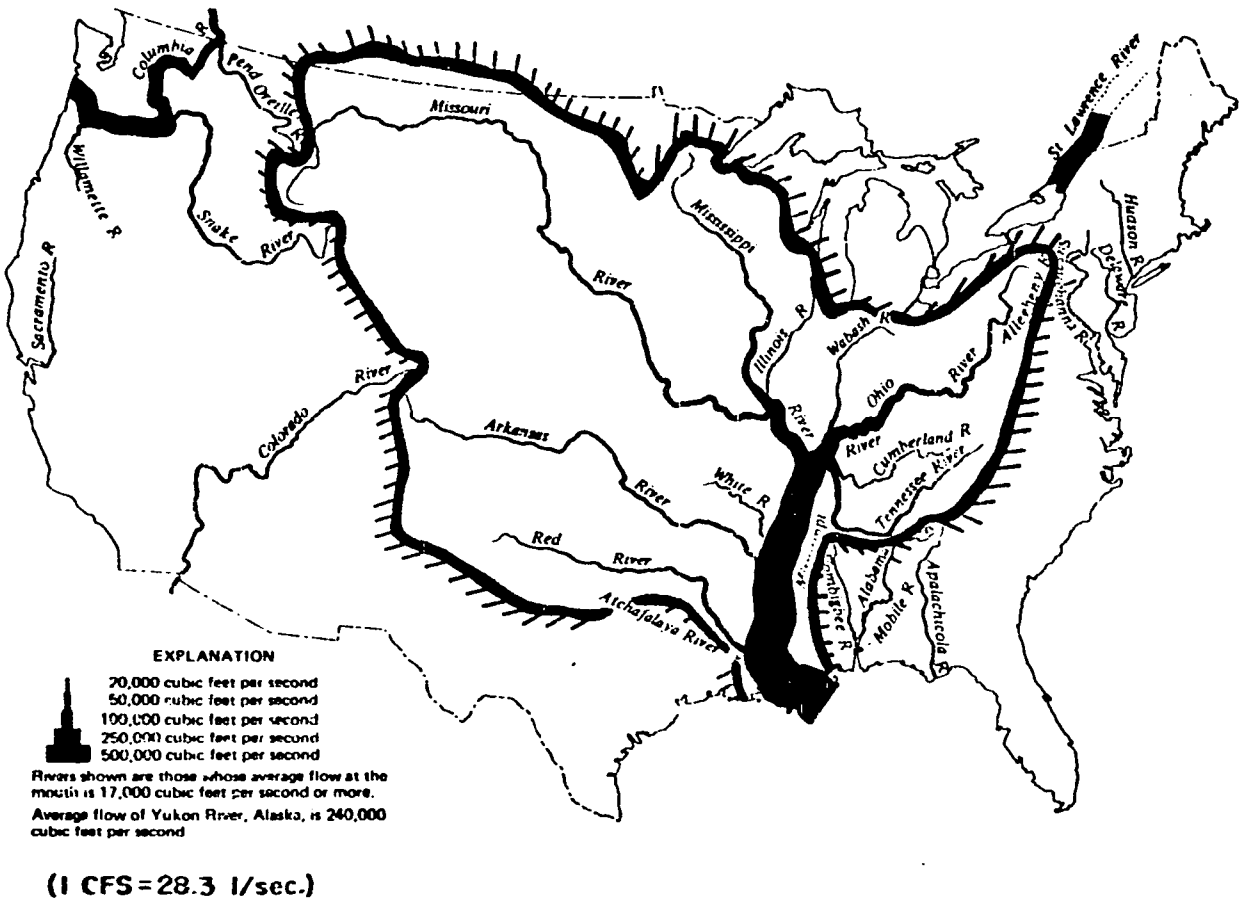


Fig. 2. Mississippi River drainage basin (map from ISERI and LANGBEIN, 1974; basin outline from JUDSON and RITTER, 1964).

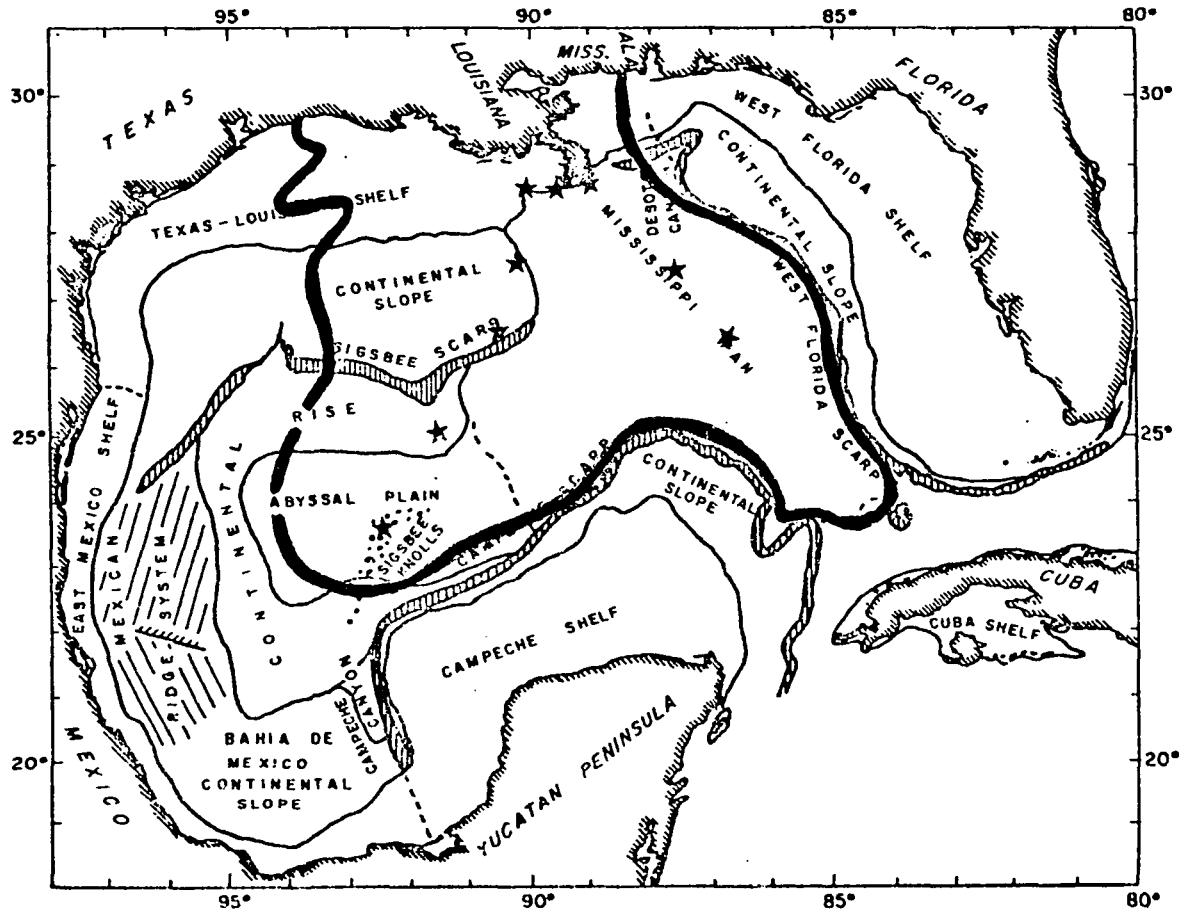


Fig. 3. Gulf of Mexico physiographic provinces with outline of Mississippi River distributive province (from DAVIES, 1972). Sampling sites of this study are indicated by ★'s.

Suspended sediment from the lower Mississippi River is typically fine-grained with no material >104μm, 1-2% between 104 and 74μm, 30-60% between 74 and 4μm, 20-30% between 4 and 1μm and 20-30% <1μm (U.S. ARMY CORPS OF ENGINEERS, 1939). The river bed-load, which is estimated to be from <10-20% of the total load (FISK et al., 1954; HOLLE, 1952), was characterized at Southwest Pass as 10-30% fine and very fine sand (250-62μm), 40-80% silt (62-4μm) and <10-50% clay (U.S. ARMY CORPS OF ENGINEERS, 1959). It follows that delta sediments are also fine-grained with reported particle-size distribution of <1-10% sand (>62μm), 25-45% silt (62-2μm) and 50-75% clay (HOLMES and HEARN, 1942; SCAFE, 1968; TIEH et al., 1973; HOTTMAN, 1975).

GRIFFIN (1962) reports that montmorillonite is the dominant clay mineral of the Western Mississippi River basin and that illite, which is found throughout the Mississippi drainage basin, is dominant in soils east of the Mississippi and north of the Ohio River. Kaolinite is the prevalent clay mineral of southern and southeastern U.S. areas. Lower Mississippi River sediments are found to have a clay mineral distribution of 50-80% montmorillonite, 10-30% illite, 10-20% kaolinite and trace chlorite (JOHNS and GRIM, 1958; GRIFFIN, 1962). Similar clay mineral distribution is also found in the Mississippi Delta sediments where there is 46-56% montmorillonite, 21-38% illite, 13-19% kaolinite and <5% chlorite (JOHNS and GRIM, 1958; MCALLISTER, 1964; SCAFE and KUNZE, 1971).

Cation exchange capacities (C.E.C.) for Mississippi River suspended clay (<4μm) are given as 49 meq/100g and for silt (61-4μm)

as 18 meq/100g (KENNEDY, 1965). West Mississippi Delta sediments (<4μm fraction) are reported to have virtually the same C.E.C. of 59 meq/100g with and without organic matter and carbonate (MCALLISTER, 1964). This is probably due to the low carbonate and organic content of these sediments (TREFRY, 1974). SCAFE (1968) shows that 55% of the delta sediment clay is <0.2μm and has a C.E.C. of 90 meq/100g with the remaining fraction (2-0.2μm) having a C.E.C. of 40 meq/100g. These values confirm the predominance of montmorillonite with the very fine clays (<0.2μm) and its presence in the 2-0.2μm fraction.

Hornblende (52%) and epidote (27%) are the most abundant heavy minerals in the Mississippi River sediments and the mineral assemblage observed in the Mississippi at Cairo, Illinois is reported to be indistinguishable from that in the Sigsbee Abyssal Plain (DAVIES and MOORE, 1970). This uniformity in the heavy mineral assemblage identifies the Mississippi distributive province shown in Fig. 3.

In summary, the Mississippi River is delivering very fine-grained, montmorillonite-rich, high C.E.C. sediment with a large surface area to the Gulf of Mexico. Such material can carry a high trace metal load (either adsorbed or in oxide coatings) and provide abundant sites for ion exchange, adsorption-desorption and redox reactions.

The Mississippi River also serves as a sink for the industrial, agricultural and municipal wastes of the central U.S. EVERETT (1971) shows, for example, that waste discharge to the river along

a 241 km stretch above New Orleans increased from 1.8 million to 18 million kg/day between 1958 and 1969. The 1969 figure of 18 million kilograms added per day is about 7% of the total dissolved load at average river flow and 21% of the total at low flow. Presumably similar situations could be shown for upper river areas near Pittsburg, St. Louis, Kansas City and Memphis. However, it suffices to say that man is measurably influencing the lower Mississippi River and that such effects must be considered in the overall river picture.

The massive sediment input of the Mississippi River has built a series of deltaic complexes over the past 6000 years, the history of which is well documented (RUSSELL, 1936; FISK, 1944; FISK et al., 1954; FISK and MCFARLAN, 1955; KOLB and VAN LOPIK, 1956; SCRUTON, 1960; COLEMAN and GAGLIANO, 1964; FRAZIER, 1967; MORGAN, 1973). The modern birdfoot (or Balize) delta (Fig. 4) is an 1800 km^2 platform on which 113 km^3 of sediment has been deposited over the past 450 years (FISK et al., 1954). The rate of subaerial land formation by the birdfoot delta, however, is about 40% lower than estimated for previous Mississippi Delta complexes. This is because most of the present-day river sediment is carried out only 3 major passes and these passes have advanced to the edge of the continental shelf and thus are depositing sediment in progressively deeper water.

Accumulation rates for the present-day deltaic sediments have been determined by COLEMAN (personal communication) and SHOKES (1976). The ^{210}Pb geochronologies of SHOKES (1976) were determined

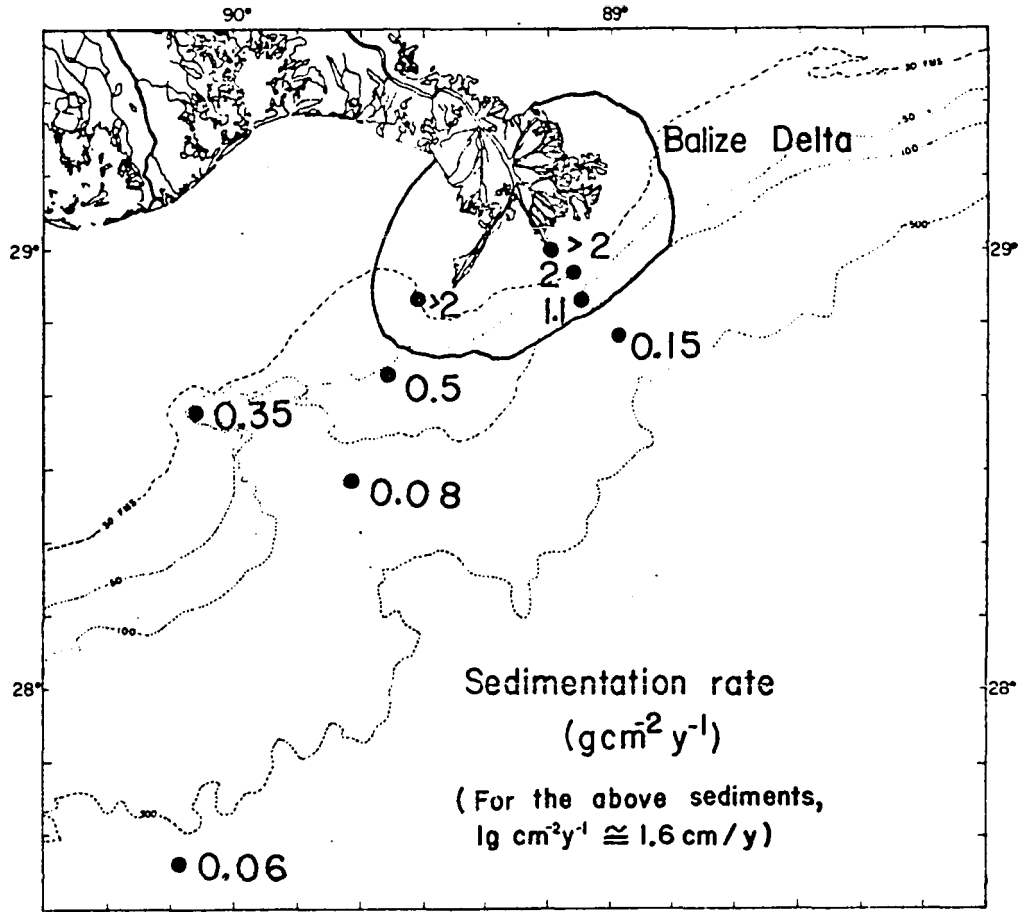


Fig. 4. Modern birdfoot or Balize delta platform (from FISK et al., 1954) with delta, upper fan and slope sedimentation rates (from SHOKES, 1976).

on the same cores used in this study and are summarized in Fig. 4. COLEMAN (personal communication), using changes in bathymetry from 1879 to 1975, finds high sedimentation rates (15-30 cm/y) in the immediate river mouth areas (∿25 m water depth) where ^{210}Pb is of limited use. On the outer delta from (70-120 m water depth) COLEMAN calculates 2-8 cm/y rates and SHOKES (1976) measures 1-2.5 cm/y. In deeper water (400-500 m) SHOKES (1976) finds rates of ∿0.2 cm/y. Although recent progradation of the delta is delivering more sediment to deeper water, sediment mass balance calculations suggest that more than 90% of the river-derived sediment is still deposited in an area that is much less than 1% of the area of the Gulf of Mexico.

Rapidly accumulating Mississippi Delta sediment is also characterized by strong reducing conditions. SHOKES (1976) showed that the rate and extent of sulfate reduction decreases away from the river mouth. Such reducing environments are highly conducive to post-depositional migration of metals. This diagenetic activity, coupled with the massive continental particulate flux to the area, make the delta an important part of the geochemical cycle.

In addition to the delta, the Mississippi province includes the Texas-Louisiana continental shelf, slope and rise, the Mississippi Fan and the Sigsbee Abyssal Plain and Knolls (Fig. 3). The shelf is a highly variable depositional environment with fine-grained fluvial sediments, delta-destructional sands and Pleistocene relict sediments (TIEH et al., 1973). It was sampled for the present study only in the immediate area west of the delta. The

other province areas were also sampled and a general description of each follows.

The Mississippi Fan covers 160,000 km^2 of the Gulf floor and is the primary reservoir for Quaternary sediments in the open Gulf of Mexico (GARRISON and MARTIN, 1973). The upper fan is characterized by Mississippi gray clay with <10% $CaCO_3$, 50-75% clay-size particles, and 45-70% montmorillonite (SCAFE and KUNZE, 1971; HOTTMAN, 1975). HOLMES (1976) found a thin surface oxidized layer of high Mn content overlying reducing upper fan sediments and related this to post-depositional migration of Mn. However, Mn-rich layers in lower fan sediments were often absent or at considerable depth in the sediments and suggest that Mn migration is not presently occurring there on a large scale. Lower fan sediments are also characterized by a 20-50 cm layer of Globigerina ooze overlying Mississippi gray lutite indicating a recent decrease in terrigenous flux to this area. HUANG and GOODELL (1970) report an eastern Mississippi Fan sedimentation rate of 30 $cm/10^3y$ with 22 $cm/10^3y$ in the upper foraminiferal layer and 34 $cm/10^3y$ in the terrigenous layer. This is considerably lower than the 100 $cm/10^3y$ and 250 $cm/10^3y$ reported for upper fan sediments (SHOKES, 1976).

Numerous salt diapirs and intraslope basins mark the gentle upper continental slope and provide sharp contrast to the precipitous Sigsbee Escarpment which descends 1000 m from the lower slope to the continental rise. Slope sediments are typically 10-20% $CaCO_3$ with lower values where large terrigenous input is found (BOUMA et al., 1976). Clay-size particles make up 60-85% of the

sediment and clay mineral distribution is reported as 20-50% montmorillonite, 30-60% illite, <6% chlorite and 7-16% kaolinite (SCAFE and KUNZE, 1971; HOTTMAN, 1975; BOUMA et al., 1976). SCAFE and KUNZE (1971) report C.E.C.'s of 75 meq/100g for the <0.2 µm fraction and 29 meq/100g for the 2-0.2µm sediment. Sedimentation rates on the slope are variable and reported values range from <10-100 cm/10^3y (BOUMA et al., 1976; SHOKES, 1976).

Stretching out from the foot of the Sigsbee Escarpment, the continental rise is covered with a thin frosting of Globigerina ooze and underlain by wedges of interbedded turbidites of slope origin (GARRISON and MARTIN, 1973). The gently sloping rise merges with the abyssal floor at about 3500 m and is similar in sediment composition to the abyssal plain.

The Sigsbee Abyssal Plain has a maximum depth of 3700 m and is virtually flat having a slope of less than 1:8000 (EWING et al., 1958). BURK et al. (1969), using a D.S.D.P. core, note that the abyssal plain sediments have a turbidite-rich sequence with pelagic sediments constituting only ¼ to <½ of the Miocene and younger sections observed. The late Pleistocene sedimentation rate is 28 cm/10^3y whereas late Miocene, Pliocene and early Pleistocene accumulation rates of 3.8-6.1 cm/10^3y were determined. KENNETT and HUDDLESTUN (1972) report a highly variable 10-20 cm/10^3y sedimentation rate with variations existing within and among cores. $CaCO_3$ concentrations are also variable and range from 15 to >40% (HARLAN, 1966; HOTTMAN, 1975). SCAFE and KUNZE (1971) report 65% clay, a C.E.C. of 81 meq/100g for the <0.2µm fraction and 41 meq/100g

for the 2-0.2μm sediment, and clay mineralogies of 36-55% montmorillonite, 31-45% illite, 2-6% chlorite and 12-16% kaolinite for abyssal plain sediments. HAGERTY (1969) and TIEH and PYLE (1972) report similar clay mineral percentages.

The flat relief of the abyssal plain is interrupted only by the Sigsbee Knolls which rise a few hundred meters above the surrounding plain. The knolls are mid-Mesozoic salt diapirs and are covered with late Miocene and younger pelagic clays and calcareous oozes (BURK et al., 1969). They provide the only opportunity of studying strictly pelagic sedimentation in the Mississippi province. The knoll cored for this work is the same as that reported for cores V3-126 and V3-128 by EWING et al. (1958). The Ewing et al. (1958) cores had a 20% coarse fraction (>74 μm) of planktonic foraminifera which decreased to <5% at 30-50 cm. Radiocarbon dating of several core sections gave the following sedimentation rates: 0-40 cm, 3.1 cm/10^3y; 40-90 cm, 7 cm/10^3y; 90-139 cm, 12.5 cm/10^3y; and 139-188 cm, 21.3 cm/10^3y. BURK et al. (1969) report a 3.0 cm/10^3y Pleistocene sedimentation rate for the Challenger Knoll and a 2.6 cm/10^3y late Pliocene sedimentation rate. Knoll sediments are reported to have 20-40% $CaCO_3$, 40-60% clay-size particles, and 20-35% montmorillonite, 30-40% illite, 10-20% kaolinite and 10% chlorite (HAGERTY, 1969; TIEH and PYLE, 1972).

In summary, the deltaic and upper Mississippi fan sediments are the primary sink for the massive input of fine-grained sediment from the Mississippi River. These rapidly accumulating sediments are low in $CaCO_3$ and organic matter, rich in fine-grained, high

C.E.C., montmorillonite clay and subject to reducing conditions. Deep Gulf sediments are a mixture of terrigenous gray lutite (presumably from turbidity flows), calcareous oozes and red-brown clay and have variable accumulation rates. It is only on the elevated Sigsbee Knolls that strictly pelagic red-brown clay and calcareous ooze are found. The Mississippi distributive province with its single sediment source, lack of hydrothermal or volcanic activity, and variety of depositional environments is thus an ideal location for study of the marine geochemistry of continental weathering products.

Previous Heavy Metal Studies: Mississippi River-Gulf of Mexico

Dissolved metal concentrations for the Mississippi River are given by DURUM and HAFFTY (1961), KOPP and KRONER (1967), DAVIS (1968), DURUM et al. (1971), U.S.G.S. (1972, 1973, 1974, 1975) and ANDREN and HARRISS (1975) and are summarized with the results of the present work on page 73. Reported concentrations vary considerably, however they are generally equal to or less than average river water values (TUREKIAN, 1969). These low concentrations are most likely due to metal adsorption on the abundant suspended matter at the relatively high river pH (7.5-8.0).

TUREKIAN and SCOTT (1967) report particulate Cr, Ag, Mo, Ni, Co and Mn concentrations for one Mississippi River sample and the U.S.G.S. (1975) gives "total" metal values for acidified unfiltered river water. However, the single observation in the former data set and variability within the latter (even when correlated with

suspended solids concentrations) point out the tremendous void that exists in our understanding of this important aspect of the Mississippi River metal load.

Dissolved metal concentrations for the Mississippi Delta and/or open Gulf of Mexico have been reported by RILEY (1937), RONA et al. (1962), SCHUTZ and TUREKIAN (1965), SLOWEY (1966), DAVIS (1968), SLOWEY and HOOD (1971), CUSTODI (1971) and ANDREN and HARRISS (1975). The most extensive work (SLOWEY, 1966; SLOWEY and HOOD, 1971) shows similar Cu and Zn concentrations for coastal and open Gulf samples yet an order of magnitude higher Mn concentrations in coastal waters. SLOWEY and HOOD (1971) also note that Mn, Cu and Zn values are higher in the Yucatan Straits than the open Gulf of Mexico and suggest that more influence is exerted by Yucatan Straits water on the metal content of the Gulf than by coastal processes. High coastal Mn values, of course, imply a significant riverine (or coastal) contribution of this metal to the Gulf. Other investigators have shown similarities in river and nearshore values for some metals (DAVIS, 1968; ANDREN and HARRISS, 1975), however, wide variations in trace element concentrations obscure any obvious trends.

Metal concentrations in northeast Gulf of Mexico suspended matter have been determined by BETZER (1975) and the major element composition of open Gulf and nepheloid layer particulates have been reported by BETZER and PILSON (1971) and FEELY (1974, 1976). Variations in the elemental composition of these particulates are often quite large and are most likely a function of the amount of aluminosilicate material, organic matter and possible contamination.

Sediment metal concentrations for the Mississippi Delta and Upper Mississippi Fan have been reported by CLARKE and STEIGER (1914), YOUNG (1954, 1968), POTTER et al. (1963), DAVIS (1968), TIEH and PYLE (1972), HOLMES (1973, 1976), TIEH et al. (1973) and TREFRY and PRESLEY (1976a). These are compiled on page 91 for later comparison with the results of the present study. In general there is remarkable agreement among the data and the values are reasonably close to those given for continental crust (TAYLOR, 1964). The early Mississippi Delta metal values (CLARKE and STEIGER, 1914; YOUNG, 1954) are still referenced by many authors (directly or indirectly) as a standard for continental detritus and nearshore sediments (WEDEPOHL, 1960; RILEY and CHESTER, 1971; GARRELS and MACKENZIE, 1971).

Some of the above investigators have shown a relationship between particle size and metal concentrations for inland and nearshore areas. YOUNG'S (1954) data show, for example, an increase in V, Ni, Co and Cr, no change in Ti and a marked decrease in Zr from inland and bay sediments (Lake Ponchatrain and Atchafalaya Bay) to Mississippi Delta and Upper Fan sediments. These changes coincide with a decrease in sediment grain size from gray silty-sand to silty-clay to clay and an increase in the percent loss on ignition (LOI). POTTER et al. (1963) found total sediment Cr, Cu, Ni, Pb and V concentrations to be higher in modern marine (Mississippi Delta) than fresh-water environments (Table 3). However, they found comparable metal values in (1) the total and <2 μm fraction of sediment from the Mississippi Delta and in (2) the <2 μm fraction of both the marine and fresh-water samples (Table 3). These observations

Table 3. Trace metal values (ppm) for five marine (Mississippi Delta) and seven freshwater argillaceous sediments (from POTTER et al., 1963)

	Marine		Fresh-water	
	Total	<2 μm fraction	Total	<2 μm fraction
Cr	72	65	31	54
Cu	33	33	15	42
Ni	42	42	21	39
Pb	24	19	12	26
V	134	157	53	120

suggest that physical fractionation is an important discriminant of metal concentrations between freshwater and marine (Mississippi Delta) sediments and that within the particle-size range of the marine sediments studied by Potter and coworkers differences in metal content due to grain size are small. Note, however, that 60-70% of delta sediment is made up of <2 μm particles and <1% contains >62 μm particles.

Considerable variation in metal content has been observed in the several sedimentary facies of the Louisiana shelf, west of the Mississippi Delta (TIEH et al. 1973; HOLMES, 1973). Highest metal concentrations and clay content are found near the delta and along the path of sediment transport from the Mississippi River. A significant covariance of Fe with several metals (Co, Cu, Cr, Mn, Ni, Pb, V and Ti) also has been observed in the delta and shelf

sediments (TIEH et al., 1973; HOLMES, 1973; TREFRY and PRESLEY, 1976a). This relationship results from the association of iron and other metals with clay-rich material either as part of the crystalline lattice or in hydrous oxide coatings. TREFRY and PRESLEY (1976a) use metal/Fe correlations to point out a large anthropogenic input of Pb and Cd to the Mississippi Delta sediments.

Metal concentrations for deep Gulf of Mexico sediments (including the Texas-Louisiana slope, lower Mississippi Fan, and Sigsbee Knolls and Abyssal Plain) have been cited by HOLMES and HEARN (1942), TRASK (1953), YOUNG (1954), WATSON (1968), WATSON and ANGINO (1969), TIEH and PYLE (1972) and HOLMES (1976) and are listed on page 139 for later reference. Enrichment of Fe and some other metals has been observed in Gulf ironstones and yellow layers (WATSON and ANGINO, 1969; PEQUEGNAT et al., 1972; MCGEARY and DAMUTH, 1973; PRESLEY, unpub. data), however, Gulf sediments usually have been presented as having relatively uniform metal concentrations.

In other attempts to identify metal enrichment in deep Gulf sediments, YOUNG (1954) found no difference in the V, Ti, Zr, Ni, Co, Sc, Cr and La values for Mississippi River derived gray clay sampled in water depths from 300 to 3400 m. TIEH and PYLE (1972) similarly observed little variation in sediment Ba, Fe, Ni, Rb, Ti, Y and Zn concentrations between nearshore and abyssal environments; yet, in abyssal samples Mn was 1.5 times higher. Most of the 20 metals studied by HOLMES (1976) in central Gulf sediments were said to be predominantly detrital and thus related to source area (e.g. Mississippi River, Bay of Campeche). HOLMES (1976) notes that abyssal plain

sediments have somewhat higher metal concentrations than basin perimeter samples and relates this to an increase in clay content. HOLMES (1976) also finds vertical variations in Mn which are indicative of post-depositional migration of Mn. WATSON and ANGINO (1969) note that Sigsbee Knoll sediments have higher Mn, Ni and Co and lower Fe concentrations ($CaCO_3$-free) than the surrounding abyssal plain.

Changes in sediment metal content on a geologic time scale have been examined by TIEH and PYLE (1972) and HOLMES (1976) who show Pleistocene metal concentrations (particularly Ti, B, V, Zr) to be higher than Recent, Pliocene or Miocene values. They relate this to increased detrital input during the Pleistocene epoch. A similar relationship of detrital input with higher metal levels was also shown for the Yucatan Shelf by ANGINO et al. (1972). WATSON and ANGINO (1969), however, concluded that Gulf of Mexico iron-rich layers formed during periods of low sediment accumulation rate from long-term exposure of surficial sediments to overlying seawater.

From the preceding discussion it seems that there are several voids and/or discrepancies in the Gulf of Mexico work. There are no substantative data on river particulate metal concentrations or metal partitioning in suspended matter and Gulf sediments. There is no data set which considers the complete spectrum of solid-phase or interstitial water metal concentrations and reactions which occur from river sources to the deep Gulf. It is not clear which metals (and to what degree) are enriched in deep Gulf sediments. This thesis addresses these problems and others in an attempt to increase our knowledge of metal geochemistry in general and as it relates specifically to the Gulf of Mexico.

METHODS

Sampling

Suspended matter, water and sediment were collected from the Mississippi River, adjacent fresh and saltwater marshes, and the Mississippi Delta region of the Gulf of Mexico during cruises in July 1973, May-June 1974, February-March 1975, July 1975, September 1975 and November 1975 (Fig. 5). Mississippi Fan and Sigsbee Abyssal Plain and Knoll sediments were taken during November 1975 (Fig. 6).

Sediments were gathered for metal, grain size, $CaCO_3$, organic carbon, and interstitial water analysis. They were collected with a plastic-lined gravity corer (2 m long, 7 cm diameter) and by sub-sampling a large box core (55 cm long, 50 cm square) using plastic tubing.

Suspended matter for metal analysis was collected in 30 ℓ Niskin bottles and recovered by vacuum filtering water through a closed system using 293 mm diameter, 0.4 μm pore size Nuclepore filters held in custom-built plastic holders. Gram quantities of particulates were obtained by processing as much as 120 ℓ of water per filter in low suspended matter areas (1-50 mg/ℓ) whereas 30 ℓ were commonly used in high suspended matter samples (50-500 mg/ℓ). The filters were stored in plastic bags and returned to the laboratory where the suspended matter was dried at 60° C and scraped off with a teflon spatula. Total suspended matter

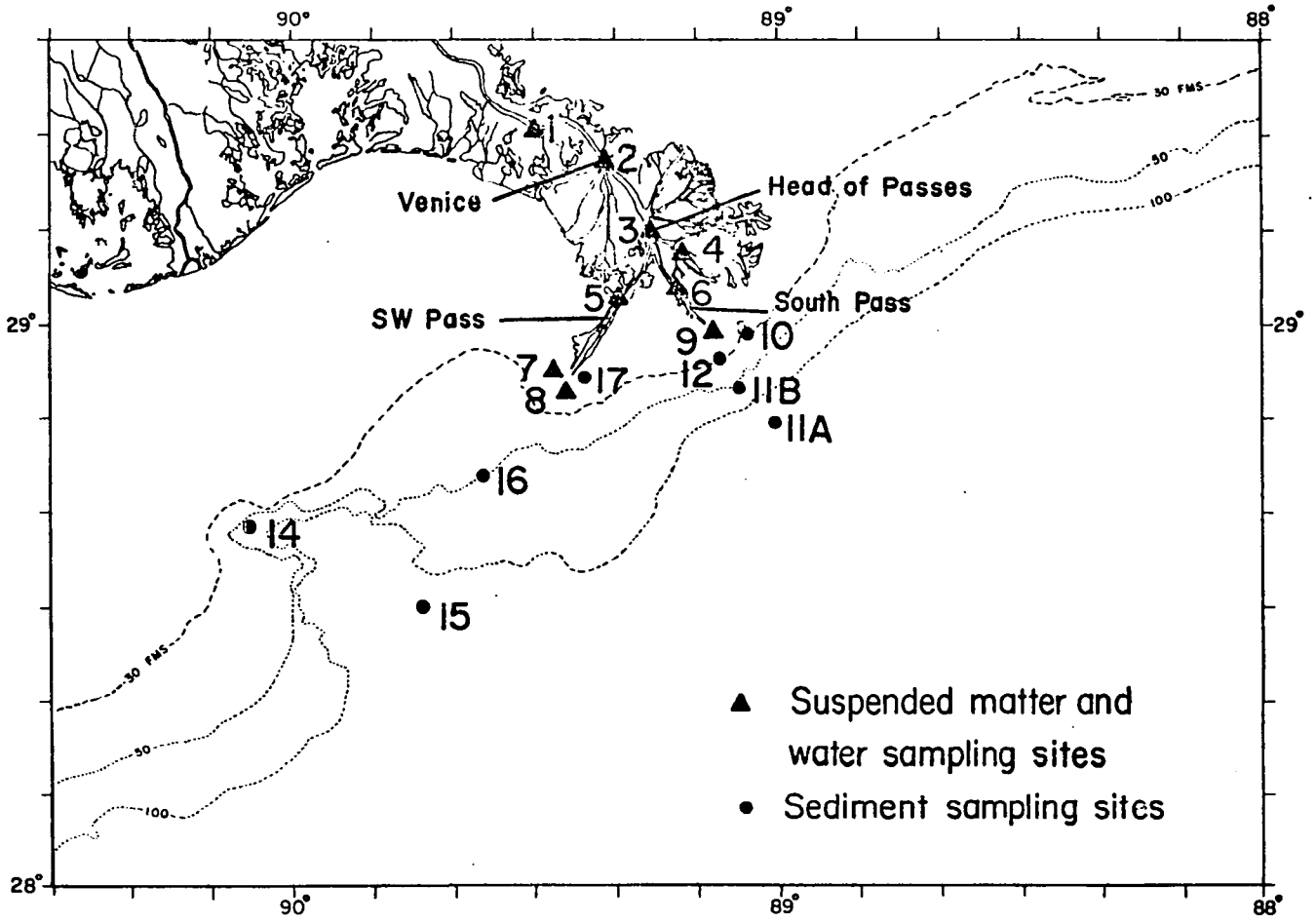


Fig. 5. Mississippi River and Delta water, suspended matter and sediment sampling sites.

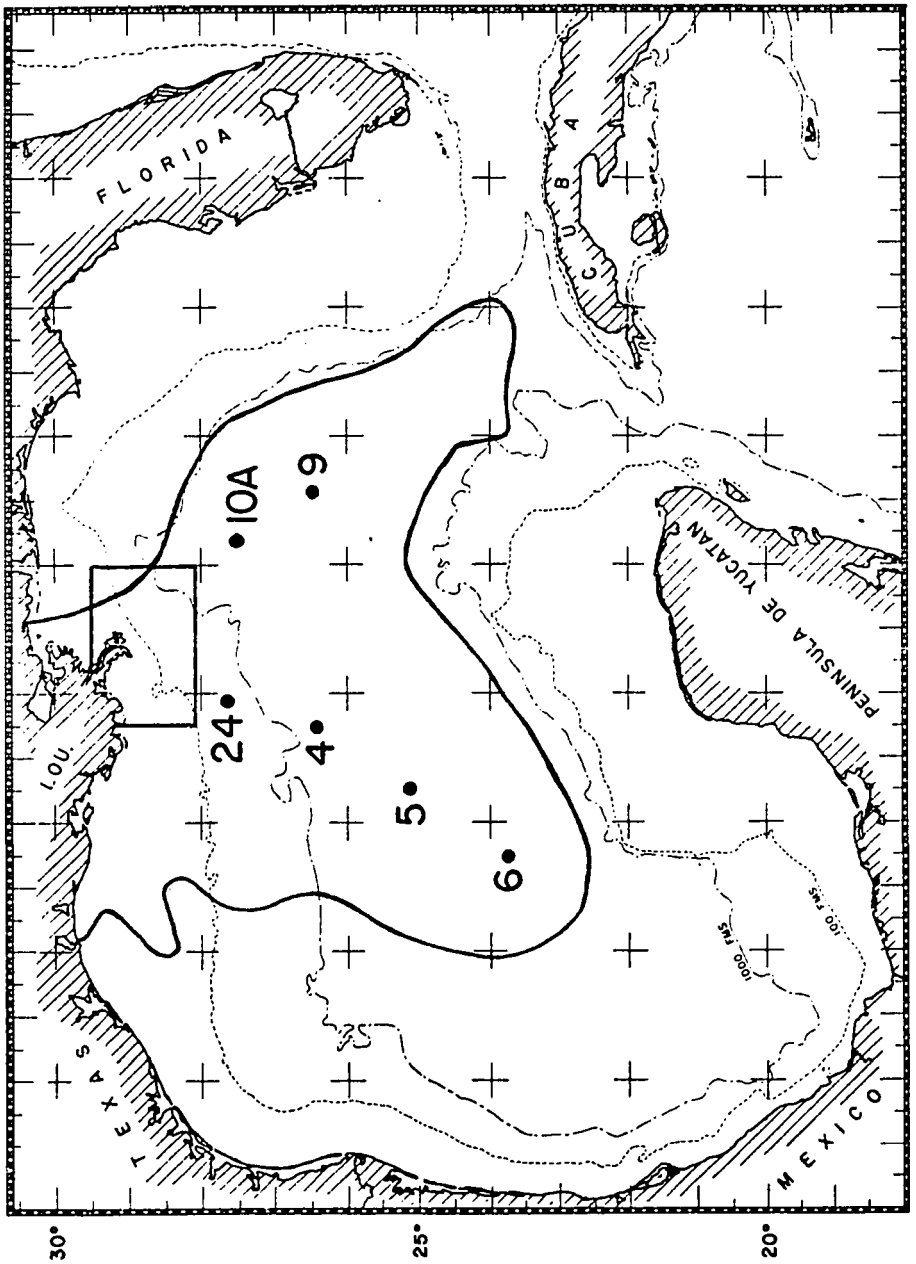


Fig. 6. Mississippi River distributive province sediment sampling sites.

(TSM) concentrations were determined at each station by filtering separate 100-1000 ml aliquots through pre-weighed 47 mm, 0.4 μm Nuclepore filters and following precautions outlined by FEELY (1974).

Water samples for dissolved metal analysis were collected separately in conventional polyethylene bottles which had been pre-soaked in 2N HNO_3 (redistilled) for several weeks. Some water samples were collected directly from the bow of a rubber boat. Others were taken by pumping water through a closed system using acid washed polyethylene tubing tied to a nylon rope and lowered from a boom extended some 10 m abeam of the ship. Most of the samples were subsequently filtered through an acid-cleaned, 47 mm, 0.4 μm Nuclepore filter apparatus and were then acidified with 1 ml of 16 N ULTREX HNO_3 per liter of sample. Many samples were stored in this manner for several months before they were analyzed, however no significant variation in concentration was measured when a given sample was analyzed at different times over a one year period.

At each station where water and suspended matter were collected, a vertical series of samples for particulate organic carbon (POC), dissolved organic carbon (DOC), dissolved silica, pH, chloride, temperature and total suspended matter was also taken.

Interstitial water for Fe, Mn and major elements analysis was squeezed from the Mississippi Delta sediment on two cruises, once using a gas-driven piston squeezer (KALIL and GOLDHABER, 1973) and once with a diaphragm squeezer (REEBURGH, 1967). Sediments were squeezed immediately after collection and the interstitial water was filtered (0.45 μm pore size Millipore filters) prior to storage. In some delta samples large amounts of Fe precipitated after squeezing and were later redissolved with acid.

Analytical Techniques

Total sediment and suspended matter metal concentrations were determined by atomic absorption spectrophotometry (AAS) following dissolution with HF and $HClO_4$. Initially, freeze-dried and powdered samples (0.3-0.5 g) were ashed at 350°C for 6-8 hours. Next the sediment was transferred to teflon beakers, 3 ml HF and 1 ml $HClO_4$ were added, and the beakers were covered with teflon watch glasses and heated for 4-5 hours. The watch glasses were then removed and the samples were brought to dryness. The acid treatment was repeated and the dried residue was redissolved with 1 ml 16N HNO_3 to which aliquots of deionized water were gradually added while heating strongly. After sufficient heating, the residue-free solution was diluted to 25 ml for analysis by AAS.

During AAS analysis, background absorbance, due to molecular absorption, was monitored by simultaneously measuring the absorbance of the analytical wavelength and that of a nearby non-resonance line. This technique was found to correct for absorbance due to a variety of matrices such as that of 10,000 ppm Ca (see APPENDIX B). Sample

matrices may also depress absorbance by promoting oxide and other compound formation. These effects were examined by carrying out method-of-additions analyses (with background correction) on a variety of sample types and are summarized in APPENDIX B. Considerable molecular absorbance was measured for several elements in some samples, however there was no detectable matrix interference for the samples analyzed in this study.

The analytical precision of the sediment metal analyses was determined by analysis of numerous quadruplicates. Precisions, expressed below as a coefficient of variation (CV), were found to be Fe, 3%; Al, 5%; Mn, 3%; Zn, 3%; Pb, 6%; Ni, 6%; Co, 5%; Cu, 5%; Cr, 12% and Cd, 15%. The accuracy of the total dissolution procedures was estimated by analyzing U.S.G.S. standard rocks. Comparisons are generally within 10% of the accepted values (see APPENDIX B).

Total sediment V and Al were determined by instrumental neutron activation analysis (INAA). Samples ($\sim$0.2 g) were irradiated for 1 minute by the 1 MW Triga reactor at the Texas A&M University Nuclear Science Center and after a 3 minute delay were counted for 5 minutes using an Ortec Ge(Li) detector and a GEOS Quanta 4096 channel pulse height analyzer. An Al flux monitor was also irradiated and counted with each sample. The ^{52}V peak at 1434 KeV and the ^{28}Al peak at 1779 KeV were converted to concentration using the program HEVESY (SCHLUETER, 1972) with U.S.G.S. standard rocks as standards. Precision was 15% for V and 1.5% for Al. Al values for 37 samples analyzed by INAA and AAS varied by an average of 3.4% (i.e. 0.26% Al).

Sediment and suspended matter samples were also subjected to a sequential series of chemical leaches similar to those of GIBBS (1973). Initially, dried and finely powdered 0.5 g samples were equilibrated with 15 ml of 1 N NH_4Cl (pH 7) on a wrist-action shaker for 18 hours to remove exchangeable metal ions. The mixture was centrifuged (@ 3000 RPM) and the solution decanted for analysis by flame or flameless AAS using standards in an NH_4Cl matrix and monitoring background absorbance. In all cases less than 1 ppm Fe was removed with the NH_4Cl indicating that iron oxides were not affected by this treatment. The sediment residue was then washed with deionized water and centrifuged prior to the second leach.

Iron and Mn hydrous oxides and associated trace metals were removed next with 15 ml of a citrate buffered (pH 4.7) $Na_2S_2O_4$ solution (COFFIN, 1963) by shaking and heating the mixture continuously for 2 hours at 60°C. Analysis of the leachates was again made with AAS using standards prepared in a pre-heated $Na_2S_2O_4$-citrate solutions and monitoring background absorbance. COFFIN (1963) has shown that the procedure does not detectably affect clay minerals nor does it completely remove Fe from magnetite, siderite, ilmenite, hematite, goethite or lepidocrocite. Furthermore, a second extraction with dithionite showed that only a small additional amount of metal could be removed (0.1-0.2% Fe, <10 ppm Mn in most cases, <1 ppm of the other metals). Considerably less than this was removed during a third extraction.

Organic matter was oxidized with 10 ml of NaOCl (pH 7) and any

resulting metal oxides were reduced with citrate-$Na_2S_2O_4$ solution for AAS analysis. Finally the remaining sediment residue was completely dissolved in HF-$HClO_4$ as previously outlined.

Grain size distribution of sediments and suspended matter was determined by the pipet method of FOLK (1968). Suspended matter was concentrated by flocculating with NaCl and centrifuging or by allowing the particulates to gravity settle. Particle size distribution for samples with a significant $CaCO_3$ content (>10%) was also determined following removal of the carbonate with a pH 5 acetate buffer to which small aliquots of 10% acetic acid were added to speed the reaction.

Carbonate content of sediment and suspended matter was determined by a modification of the method of PRESLEY (1975). Modifications included (1) replacing the reaction vessel valve with surgical tubing and a pinch clamp to reduce leakage and (2) freezing the sample in liquid N_2 and measuring the pressure at the end of each run as a check on possible air influx during analysis. Precision for samples with $\sim$2% $CaCO_3$ was $\sim$6% and for other samples <2.5%.

Sediment organic carbon was determined manometrically using a LECO induction furnace to combust pre-acidified samples (YOUNG and LINDBECK, 1964). Precision for the analyses was $\sim$6%.

River dissolved metal concentrations were analyzed in most samples by direct injection into a flameless atomic absorption spectrophotometer (Perkin Elmer 306 with an HGA 2100). Some analyses were made by solvent extraction with pre-cleaned ammonium

pyrollidine dithiocarbamate (APDC) and methyl isobutyl ketone (BROOKS et al., 1967). Metals complexed by the APDC were back-extracted into 1 N ULTREX HNO_3 for atomic absorption analysis. BARNARD and FISHMAN (1973) and EDMUNDS et al. (1973) have compared direct analysis versus extraction for freshwater and concluded that Fe, Cr, Cu and Mn may be successfully analyzed directly. This study has shown by solvent extraction and/or method-of-additions analysis that the above four metals may be analyzed directly in Mississippi River water. Pb and Cd values were less reliable when determined by direct analysis. Nickel concentrations were not high enough in any of the samples to allow direct analysis.

Water samples with >250 mg/ℓ dissolved solids were analyzed only after solvent extraction. The extraction method was checked by carrying out second and third extractions and by spiking raw and extracted samples. Precisions (CV) for water analyses were Fe, 15%; Mn, 15%; Cr, 5%; Cu, 12%; Pb, 20%; and Cd, 30%.

Iron and Mn concentrations in interstitial water were determined by flame AAS following a 1:4 dilution with deionized water. Standards were prepared in Copenhagen seawater of comparable ionic strength. Precisions for these analyses (CV) for concentrations >1 µg/ml were ~4%.

Chlorinity, dissolved silica and pH of the water samples were determined by standard titrametric, colorometric and electrometric methods respectively (STRICKLAND and PARSONS, 1972). Particulate and dissolved organic carbon content were measured by the wet combustion infrared methods of FREDERICKS and SACKETT (1970).

RESULTS AND DISCUSSION

The Mississippi River Metal Flux

This section characterizes the metal load of the Mississippi River. In doing so, it provides a reference point for discerning chemical alterations which occur as river material passes into the Gulf of Mexico. Specifically, the section presents the chemical composition of the dissolved and suspended fractions along with data from chemical partitioning of the particulate metals into various phases or modes of transport. The total dissolved and particulate metal flux from the river to the Gulf of Mexico is also determined and the effect of river hydrological conditions on this flux is considered. Furthermore, river suspended matter chemistry is compared with that of continental crust to contrast the composition of weathering products with likely parent material. Once characterized, this riverine source material is compared in later sections with Mississippi Delta suspended matter and sediments and deep Gulf of Mexico sediments. This comparative approach provides a direct measure of chemical changes which occur as continental detritus is subjected to the marine environment.

River Hydrological Conditions

Mississippi River suspended sediment and water discharge data from measurements at Tarbert Landing, Mississippi (493 km above Head of Passes) during the period of this study are presented in Fig. 7. Water flow ranged from 5.3×10^6 to 34.4×10^6 ℓ/sec,

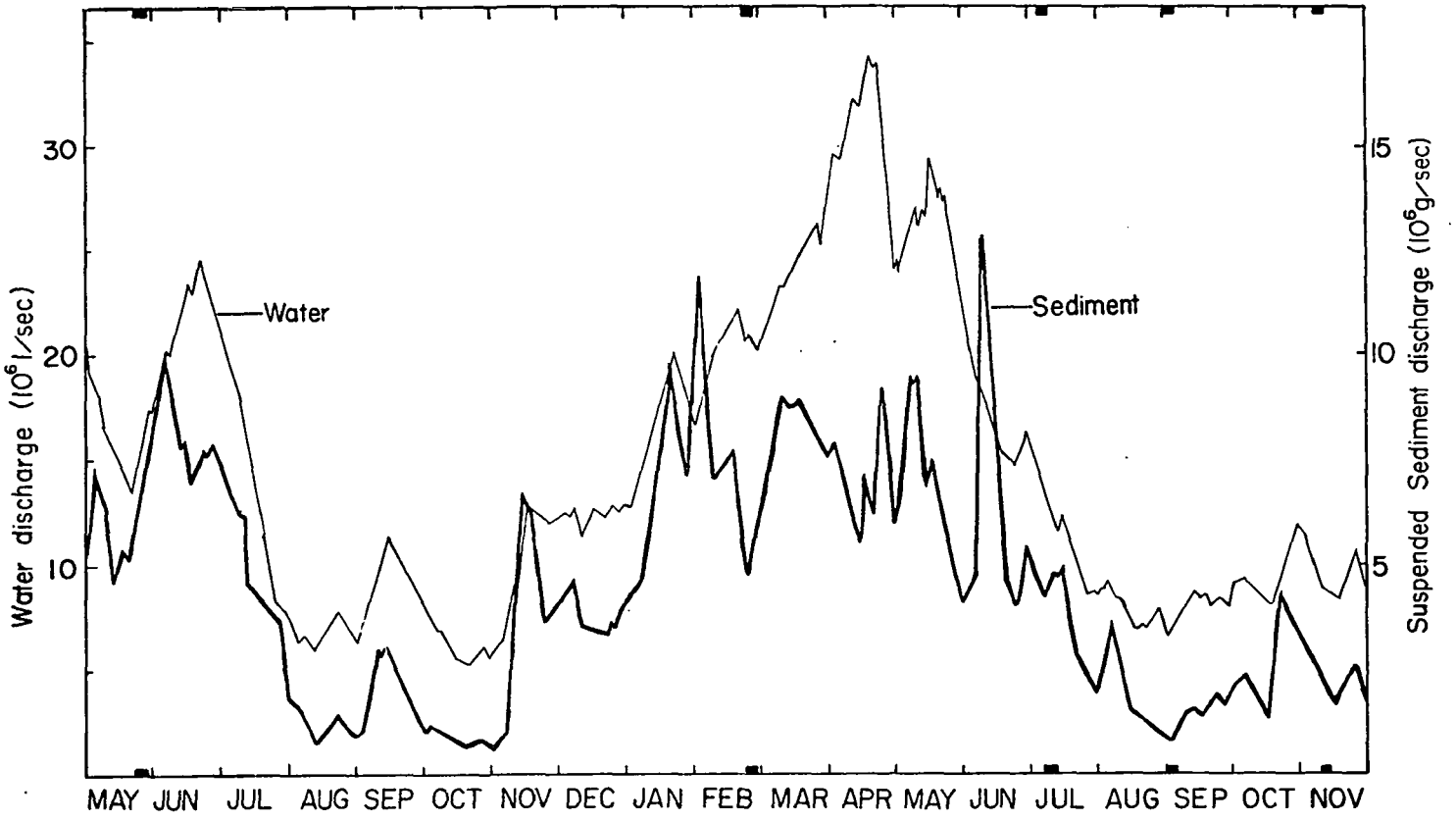


Fig. 7. Mississippi River water and suspended sediment discharge at Tarbert Landing, Mississippi for the duration of this study (May 1974-November 1975) with sampling periods blocked in along the baseline (Data from U.S. ARMY CORPS OF ENGINEERS, 1974-1975).

suspended sediment discharge from 0.7×10^6 to 12.8×10^6 g/sec and suspended sediment concentrations from 120 to 710 mg/ℓ (U.S. ARMY CORPS OF ENGINEERS, 1974, 1975). These data were obtained by measuring water flow and suspended sediment concentrations at 40 discrete positions of a river cross section and are the result of a highly refined quantitative effort. Because Tarbert Landing is below the control channel which diverts part of the Mississippi flow to the Atchafalaya River, Fig. 7 depicts only about two-thirds of the total load of the Mississippi-Atchafalaya River system.

Water flow during the 1974-1975 period followed the typical annual pattern of low flow in late summer with a slow rise, flood crest and gradual falling over the remaining months. In general, suspended sediment discharge is directly related to water flow; however the sediment load is usually higher during a rising than a falling stage and peak sediment discharge usually occurs before peak water flow. These observations, which can be seen in Fig. 7, are a function of the availability of particles for transport and the velocity and turbulence of the river (EVERETT, 1971).

Total suspended matter (TSM) data obtained during the five sampling cruises of this study are consistent with the above trends (Table 4). For example, during May-June 1974 and July 1975 the river was near average flow and sediment discharge, yet in February-March 1975, a period of above average flow, a lower sediment load was observed because the river had been at high flow for several weeks. During the September 1975 cruise the river was at its annual low stage and TSM concentrations (11 mg/ℓ) were much lower

Table 4. Hydrological conditions at Mississippi River sampling stations (Mean and standard deviations for samples analyzed)

Dates of Collection	Sample Location (Fig. 5)	River* Discharge (10^6 ℓ/sec)	Sediment* Discharge (10^6 g/sec)	Cl (mg/ℓ)	pH	Temp. (°C)	DOC‡ (mg/ℓ)	POC‡ (mg/ℓ)	TSM‡ (mg/ℓ)	POC/TSM (%)	Dissolved Silica (μM)	Suspended Clay (% of TSM)	Suspended Silt (% of TSM)
29 May - 2 Jn. 1974	(2,3,5,6)	16.4	7.3	21 (±1)	-	23.9 (±0.4)	-	1.49 (±0.27)	220 (±57)	0.73 (±0.27)	90 (±1)	48.9 (±4.2)	51.0 (±4.4)
26 Feb. - 1 Mar. 1975	(2-6)	21.2	5.4	19 (±1)	-	10.0 (±0.2)	3.58 (±0.54)	1.70 (±0.30)	156 (±32)	1.14 (±0.20)	105 (±2)	58.6 (-)	40.9 (-)
10-14 July 1975	(1-3)	13.3	4.5	27 (±2)	8.10 (±0.05)	28.0 (-)	3.33 (±0.20)	2.10 (±0.78)	231 (±111)	0.93 (±0.21)	-	66.4 (±1.9)	33.4 (±1.8)
7-9 September 1975	(1,3)	6.8	0.9	31,240	8.00 (±0.02)	21.4 (-)	3.22 (±0.16)	0.92 (±0.10)	11.0 (±1.3)	8.2 (±0.8)	18.8 (±1.6)	-	-
16-17 November 1975	(2,3,5,6)	8.8	3.2	-	7.74 (±0.03)	17.9 (±0.1)	2.72 (±0.7)	1.12 (±0.17)	38.3 (±11.5)	2.8 (±0.7)	91 (±7)	-	-

* Data from U.S. ARMY CORPS OF ENGINEERS (1974, 1975) for Tarbert Landing, Mississippi; corrected to Head of Passes using appropriate time lag and converted to metric units.

‡ DOC = dissolved organic carbon; POC = particulate organic carbon; TSM = total suspended matter.

Note: the complete hydrologic data set is given in APPENDIX C.

than at other times. Note, however, that downstream river suspended sediment concentrations measured in September 1975 (11 mg/ℓ, this study; 23 mg/ℓ, U.S.G.S., 1975) and November 1975 (38 mg/ℓ, this study; 24 mg/ℓ, U.S.G.S., 1976) were much lower than predicted from the Tarbert Landing data (132 mg/ℓ for September and 364 mg/ℓ for November). This downstream decrease at low flow results from insufficient river energy to maintain a high particulate load. The opposite effect, due to river scouring, should be observed on commencement of high river flow. Unfortunately, sampling periods for this study did not overlap with any of the brief episodes of high sediment flux (Fig. 7). However, even TSM data reported in Table 4 for average or above average flow are 1.5 to 2 times lower than the projected Tarbert Landing values. This may be due to the incomplete river cross section sampled, a decrease in river energy and suspended sediment concentrations below Venice where the levee system ends and river distributaries begin, and perhaps an increase in the near-bottom sediment load.

Suspended sediment transport in the lower Mississippi River is controlled by the river velocity profile, salinity and temperature, and river stage and tidal influences with their associated salt wedge. Several investigators have discussed these parameters in detail (U.S. ARMY CORPS OF ENGINEERS, 1939, 1956; HENRY, 1961; and EVERETT, 1971) and thus only a few representative TSM profiles for the lower river and passes are presented here (Fig. 8). Figs. 8a-d show both the seasonal variability in suspended sediment

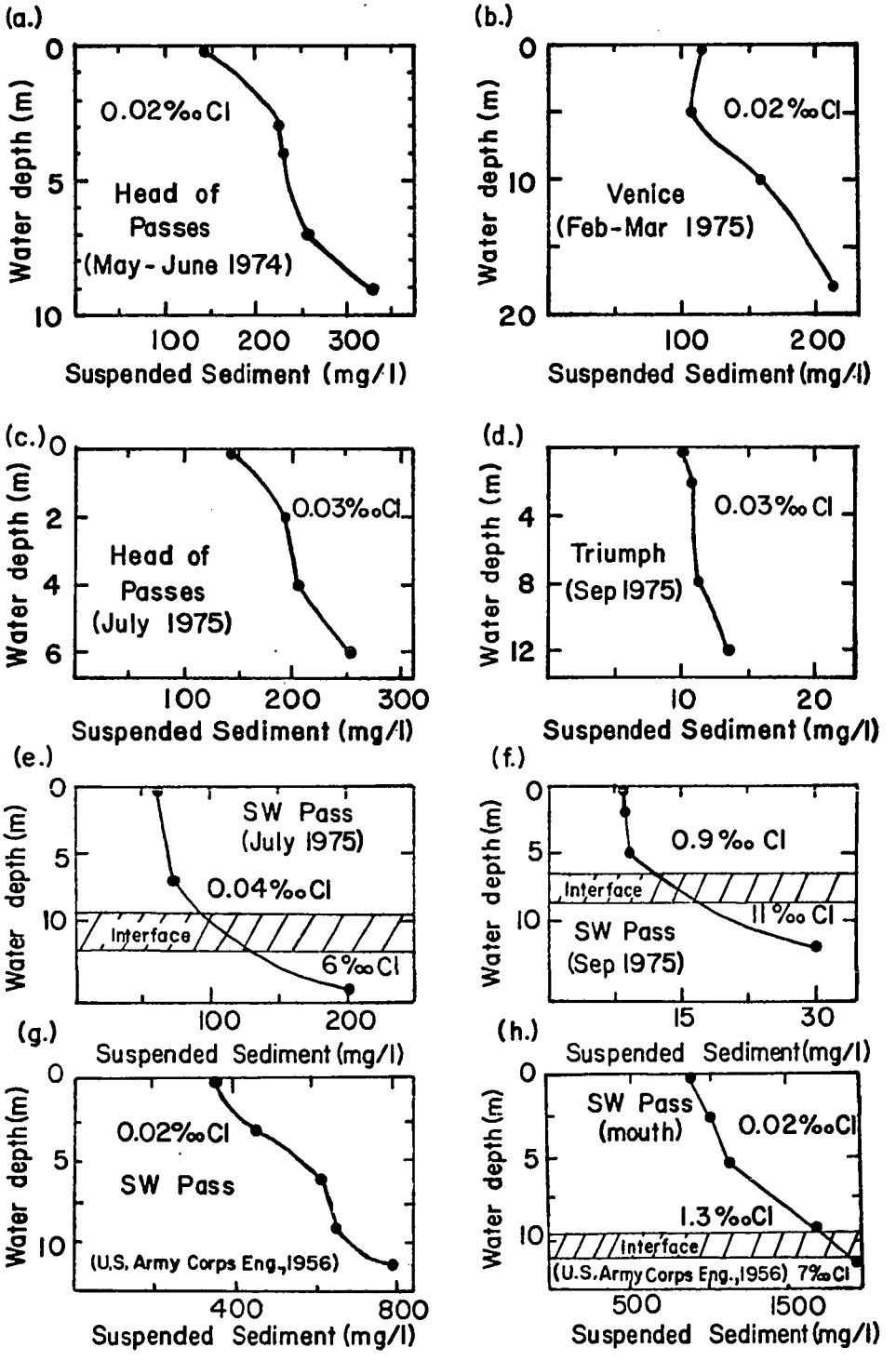


Fig. 8. a-h. Lower Mississippi River suspended sediment profiles from this study (Figs. a-f) and that of the U.S. ARMY CORPS OF ENGINEERS (1956, Figs. g and h).

concentrations and the commonly observed surface TSM minimum and near-bottom TSM maximum. Figs. 8e and 8f show the decrease in surface particulate concentrations and the constant or increased near-bottom load found in the distributary passes. Finally, Figs. 8g and 8h show high values that have been measured during periods of peak sediment flux.

Clay (<2 μm) and silt (62.5 μm-2 μm) size particles made up virtually the entire mass of suspended matter collected during this study (Table 4). This agrees well with the previously cited U.S. ARMY CORPS OF ENGINEERS (1939) data, yet due to the predominance of surface water samples analyzed is perhaps more skewed toward clay particles than the typically reported 50% clay, 48% silt, 2% sand (GAGLIANO and VAN BEEK, 1970). Nevertheless, the fine-grained character of the Mississippi suspended load is evident.

Mississippi River dissolved solids concentrations (measured at Luling Ferry, Louisiana; 193 km above Head of Passes) have an annual range of 172 to 326 mg/ℓ and average 247 mg/ℓ (LEIFESTE, 1974). River chloride concentrations (Fig. 9) generally range from 10-50 mg/ℓ (U.S.G.S., 1974, 1975) and are directly comparable to total dissolved solids data and inversely related to river flow. River water chlorinities measured for this study were uniform during any given sampling period, and ranged from 19-31 ppm over the five cruises with seasonal variations being inversely related to water flow. Upstream salt intrusion was observed during September and November and to a lesser degree during July (see Appendix C for complete hydrographic data). Dissolved silica concentrations were

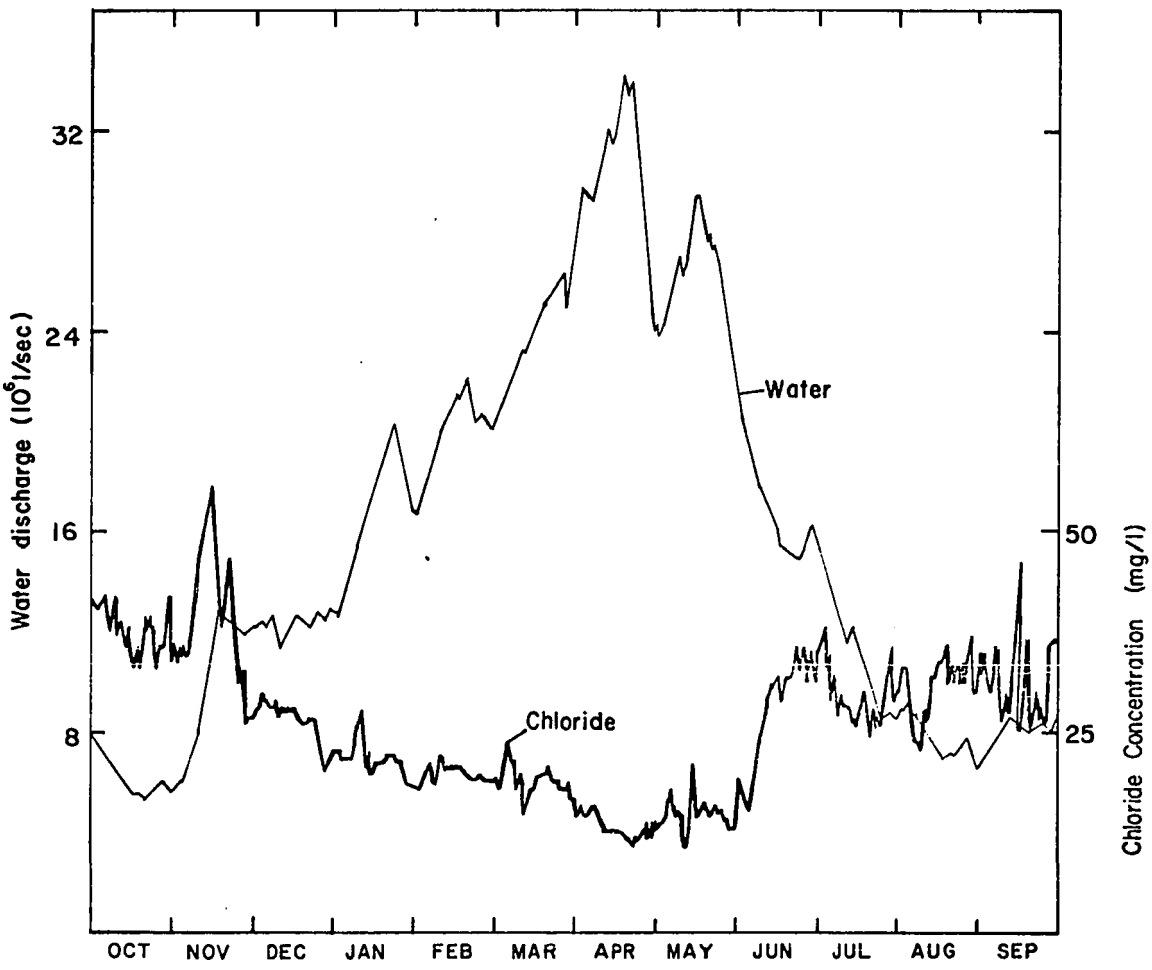


Fig. 9. Mississippi River chloride concentrations at St. Francisville, La. (U.S.G.S., 1975) and water discharge at Tarbert Landing, Miss. (U.S. ARMY CORPS OF ENGINEERS, 1975) for October 1974 to September 1975.

also spatially uniform in the river and ranged from 87-108 μM over the four normal flow periods. However, an average of 19 μM was measured for September when suspended matter concentrations were only 11 mg/ℓ.

River pH was high and uniform in the lower river with values ranging from 7.74-8.15 over the entire study period. Temperature varied from 10-28°C during the five cruises, yet was also uniform at any given time.

Dissolved organic carbon (DOC) concentrations were essentially the same for all seasons with an overall average of 3.33 ± 0.45 mg C/ℓ. Particulate organic carbon (POC) was, of course, variable as a direct function of the suspended load of the river and ranged from 0.82-3.73 mg C/ℓ. POC/TSM values, however, are a better indicator of the relative importance of particulate organic carbon and these values ranged from 0.48-1.32% during May-June, February-March, and July. Markedly higher values of 7.5-9.3% were measured during September when the river was at its annual low stage.

During most of the year the Mississippi River (above Head of Passes) is a uniformly mixed water mass, varying only in the vertical stratification of the suspended load. Variations in dissolved constituents, suspended sediment concentrations and percent particulate organic carbon can be considerable on a yearly basis as a function of river stage. These observations are inherent in making total metal flux calculations and in explaining discrete metal observations.

River Particulate Metals

Average metal concentrations in river particulates (Table 5) varied only slightly over the first three sampling periods when the river was at or above mean flow. Concentrations for the November 1975 samples were also similar to the first three; however the September samples were atypical and will be considered separately. Differences in metal concentrations among samples from several river locations and depths were generally small as is shown by the standard deviation given for each period (Table 5) and by scanning the complete data set (APPENDIX D). Occasional variations observed were usually for the entire spectrum of metals including Fe and Al, suggesting that there are minor differences in river suspended matter surface coatings and mineralogical composition. For example, Cruise 75-G-1 data (APPENDIX D) show that maximum Fe (5.13%), Al (9.18%), Zn (202 ppm), Cu (46.2 ppm), Ni (62.7 ppm) and Cd (1.5 ppm) were for the same sample (SW Pass surface, 12 km below Head of Passes) whereas minimum Fe (4.26%), Al (8.10%), Zn (52 ppm), Cu (35.8 ppm), Ni (52.0 ppm) and Cd (1.0 ppm) were observed for surface and 7 m samples upstream at Venice (16 km above Head of Passes). The above data also point out probable physical sorting of particulates as they are transported downstream.

Somewhat higher metal values found for May-June 1974 samples (Table 5 and APPENDIX D) may be due to a bias toward finer grained material resulting from draining the Niskin bottles from the lower side rather than from the very bottom. This effect was shown by comparing Niskin sample data with that from samples collected in

Table 5. Mississippi River suspended sediment metal concentrations

Cruise	No. of Samples (locations)*	River Discharge† ($x10^6$ ℓ/sec)	Sediment Discharge† ($x10^6$ g/sec)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	POC/TSM (%)	TSM (mg/ℓ)	Silt (%)	Clay (%)
74-G-9 29 May-2 June 1974	11 (2,3,5,6)	16.4	7.3	4.82 (±0.27)	8.79 (±0.37)	1400 (±50)	201 (±11)	50.8 (±5.9)	41.7 (±2.0)	20.4 (±2.1)	-	58.9 (±2.7)	1.3 (±0.1)	0.76 (±0.37)	230 (±54)	48.9 (±4.2)	51.0 (±4.4)
75-G-1 26 Feb.-1 Mar. 1975	11 (2,3,5,6)	21.2	5.4	4.66 (±0.32)	8.63 (±0.32)	1190 (±50)	177 (±15)	42.9 (±4.6)	40.1 (±3.5)	19.6 (±1.4)	80 (-)	57.0 (±3.3)	1.2 (±0.2)	1.12 (±0.21)	146 (±28)	40.9 (-)	58.6 (-)
75-G-8 10-14 July 1975	9 (1,2,3,5)	13.3	4.4	4.61 (±0.12)	8.91 (±0.32)	1330 (±70)	175 (±17)	42.4 (±5.1)	44.3 (±2.9)	21.8 (±2.1)	79 (±3)	52.6 (±4.2)	1.2 (±0.1)	0.93 (±0.21)	217 (±117)	33.4 (±1.8)	66.4 (±1.9)
75-G-11 7-9 September 1975	4 (1,3,5,6)	6.8	0.9	3.48 (±0.35)	6.60 (±0.36)	1730 (±180)	255 (±6)	43.4 (±1.8)	61.6 (-)	18.5 (±0.6)	-	49.2 (±3.9)	2.2 (±0.2)	8.3 (±0.8)	10.2 (±1.4)	-	-
75-G-16 16-17 November 1975	8 (2,3,5,6)	8.8	3.2	4.70 (±0.13)	9.06 (±0.31)	1180 (±70)	210 (±28)	47.8 (±3.6)	51.5 (±6.8)	-	-	54.6 (±3.1)	1.2 (±0.5)	2.8 (±0.8)	40 (±10)	-	-
	43	Mean (std. dev.)		4.61 (±0.40)	8.65 (±0.70)	1300 (±180)	193 (±29)	46 (±6)	45 (±7)	21 (±2)	79 (±3)	55 (±4)	1.3 (±0.4)	2.0 (-)	149 (±105)	40.8 (±8.7)	59.0 (±8.7)

* Locations: 1 Triumph; 2 Venice; 3 Head of Passes; 5 SW Pass; 6 So. Pass; See Fig. 5, p. 30.

† Data from U.S. ARMY CORPS OF ENGINEERS (1975, 1976).

Note: Complete river suspended matter data set is given in APPENDIX D.

plastic carboys directly from the river surface. The latter sample concentrations were 10-15% lower for the May-June 1974 samples, yet the two sampling techniques gave similar values for the July 1975 cruise when water was drained from the bottom of the Niskin bottles (see APPENDIX D). The above comparisons also help to reassure that significant contamination was not encountered during collection of the river suspended matter.

The overall consistency of metal content for the four "average" data sets is also reflected in the chlorinity, pH, DOC, POC/TSM, and silica data but is not well reflected in the TSM values (Tables 4 and 5). TSM ranged from 38-500 mg/ℓ, however Fe concentrations varied only between 4.26 and 5.13% and the extremes for the other metals were not large (Al, 8.10 to 9.39%; Ni, 49.2 to 62.7 ppm; Cu, 35.6 to 49.1 ppm; Co, 18.1 to 24.8 ppm; Pb, 35.0 to 62.4 ppm; Mn, 1110 to 1480 ppm; Cd, 0.8 to 1.5 ppm; Zn, 152 to 249 ppm). Thus within this large TSM range, there are generally minor variations in particulate metal composition.

Metal concentrations for river suspended matter collected at low flow showed several differences relative to the other periods. Hydrological conditions were also different at low flow. TSM (11 mg/ℓ) and dissolved silica (19 μM) were markedly lower but the POC/TSM ratio (8.3%) and chloride concentrations (at Head of Passes) were considerably higher. Particulate Fe and Al concentrations were about 25% lower in September than the average of the other four periods whereas Mn, Zn and Cu were 30-40% higher. There was no significant difference in Pb, Ni and Co concentrations but the

Cd concentrations were 80% higher during low flow. The decreased Fe and Al content in the low flow samples is probably due to simple dilution by organic matter which keeps the Fe/Al ratio for these samples (0.527) statistically the same as that for the previous sets (0.533). Mississippi River particulate organic matter is 25-35% C (JEFFREY, personal communication) and thus the difference between 24-33% particulate organic matter during September relative to 2-6% for the other periods is sufficient to account for the 25% lowering of Fe and Al. Increased Mn, Zn, Cu and Cd concentrations at low flow suggest some association of these metals with the increased organic matter or with oxide coatings on the greater surface area of the fine-grained material being carried at this time.

Data from CARPENTER et al. (1975) also show higher metal concentrations in the Susquehanna River particulates during periods of low flow, and these too were related to increased organic matter content. However, the order-of-magnitude range in trace metal concentrations reported by Carpenter was not observed in the Mississippi River. This may be due to the greater water flow and sediment discharge of the Mississippi which make it less sensitive to man-introduced metals or other perturbances.

Organic-carbon/metal correlations as well as several other significant (at $p<0.01$) interelement relationships for the Mississippi River suspended matter are evident from the correlation coefficients matrix given in Table 6. Iron, Al and Ni show a negative covariance with organic matter whereas Mn, Zn, Cu and Cd are

Table 6. Correlation coefficients matrix for Mississippi River suspended matter data*

	Z	Fe	Al	Mn	Zn	Pb	Cu	Co	Ni	Cd	Silt	Clay	Cl	TSM	$\frac{POC}{TSM}$
Z†	1.00														
Fe	-	1.00													
Al	-	0.86	1.00												
Mn	-	0.49	-0.62	1.00											
Zn	-	-	-	0.43	1.00										
Pb	-	0.44	-	-	0.43	1.00									
Cu	-	-0.40	-	-	0.79	-	1.00								
Co	-	0.38	0.44	-	-	-	-	1.00							
Ni	-	0.58	-	-	-	0.43	-	-	1.00						
Cd	-	-0.49	-0.55	0.68	0.55	-	0.56	-	-	1.00					
Silt	-	-	-	-	-	-	-	-	0.93	-	1.00				
Clay	-	-	-	-	-	-	-	-	-0.93	-	-1.00	1.00			
Cl	-	-	-	-	-	-	-	-	-	-	-	-	1.00		
TSM	0.45	-	-	-	-0.49	-	-0.52	-	-	-	-	-	-	1.00	
$\frac{POC}{TSM}$	-	-0.75	-0.75	0.43	0.73	-	0.84	-	-0.41	0.65	-	-	0.74	-0.70	1.00

* Only correlations significant at $p < 0.01$ are listed.

† Z = water depth.

positively related. Interrelement relationships involving these elements are similarly grouped. These associations suggest that there are two metal subsets which differ in the relative amounts of organically-chelated and/or dissolved species available for adsorption on the fine-grained low river stage particulates. They also suggest basic differences in chemical partitioning or modes of particulate metal transport, a topic to be considered presently.

High Ni/silt covariance (Table 6) is not biased by extreme values and suggests that Ni is found with silt-size particles and their associated minerals. The correlation matrix also reaffirms previously discussed positive depth/TSM and POC/Cl relationships and negative TSM/organic-matter covariance. Application of other statistical parameters (factor and cluster analysis) did not enhance any of the previously stated observations and thus are not included for this data set.

Chemical leaching of particulates reveals, in a general way, the modes of suspended metal transport by the river. It identifies metals which are exchangeable, associated with Fe and Mn oxides and organic/sulfide compounds and in silicate and other mineral crystal lattices. Although chemical partitioning is not completely definitive as to the exact nature of the phase attacked in each case, it does allow relative examination of metal distribution in different sediment types.

A brief restatement of the sequential chemical leaching method used follows. The initial 1 N NH_4Cl treatment (at pH 7) removes only metal ions which are exchangeable (Exch.) with the ammonium ion

at an ionic strength which is slightly greater than that of seawater. Citrate buffered sodium dithionite ($Na_2S_2O_4$, pH 4.7), the second solution used, removes reducible (Red.) "free" iron and manganese oxides with their associated adsorbed or coprecipitated metals. Sodium hypochlorite (NaOCl, pH 7) the third solution used, removes oxidizable (Ox.) organic matter and sulfides and metals associated with these phases. Finally, after the surface has been thrice attacked, residual (Res.) silicate and other crystalline minerals and their metals are dissolved in $HF-HClO_4$. This final, most resistant phase should be least subject to alteration in the marine environment whereas each of the other phases may be more susceptible. To avoid the confusion sometimes associated with chemical partitioning discussions, note that for each of the four leaches carried out, the following identifications will be used interchangeably: (1) exchangeable (Exch.) and NH_4Cl-removable; (2) reducible (Red.), oxide (or "free" oxide) phase, and $Na_2S_2O_4$-removable; (3) oxidizable (Ox.) and NaOCl-removable; (4) residual (Res.) and lattice-held.

Table 7 gives the leachable metal concentrations and percent of total metal removed from the river suspended matter by each chemical treatment. Overall, metals were predominantly in the "free" oxide and crystal lattice phases. There was generally good agreement between the sum of the metal concentrations for the sequential leaches and the total concentration determined independently (Table 7).

NH_4Cl removed <2 ppm Fe or <0.01% of the total Fe present in the river suspended matter. This demonstrates the well oxidized, tightly bound nature of the particulate Fe. Iron oxide concentrations (Red.

Table 7. Chemical partitioning of metals in Mississippi River particulates

Sampling period	Location*	Water depth	POC / TSM (%)	Fe ( ) Red.	Ox.	Res.	Total (sum)	Total	Mn (ppm) Exch.	Red.	Ox.	Res.	Total (sum)	Total	Cu (ppm) Exch.	Red.	Ox.	Res.	Total (sum)	Total
	3	sfc	0.7	2.75	0.29	2.01	5.05	5.09	89	1278	31	111	1509	1419	0.8	11.2	15.2	14.6	41.8	41.1
May-June	3	9m	0.7	2.64	0.31	1.95	4.90	4.90	96	1171	33	113	1413	1350	0.5	10.1	15.1	12.9	38.6	42.2
1974	5	5m	-	2.78	0.30	2.01	5.09	4.94	80	1186	33	113	1412	1386	0.5	10.9	16.7	16.3	44.4	42.4
	6	7m	0.5	2.53	0.31	2.08	4.92	4.51	75	1220	35	108	1438	1455	0.2	10.8	14.0	16.2	41.2	38.6
Feb-Mar	3	sfc	1.3	2.49	0.25	1.85	4.59	4.53	110	986	27	113	1236	1200	0.5	10.5	12.3	14.7	38.0	37.4
1975	3	6m	-	2.45	0.25	2.09	4.79	4.60	78	1020	24	114	1236	1250	1.2	13.5	14.4	9.0	38.1	40.0
July	3	sfc	1.0	2.11	0.31	2.39	4.81	4.55	45	1195	34	118	1392	1348	0.6	22.4	13.2	11.6	47.8	48.1
1975	3	4m	0.9	2.20	0.33	1.95	4.48	4.46	48	1192	37	107	1384	1374	0.4	16.5	14.4	16.1	47.4	49.1
September	3	sfc	7.7	1.70	0.19	1.76	3.65	3.30	300	1463	36	85	1884	1854	-	-	-	-	-	-
1975	3	5m	7.5	1.97	0.16	1.26	3.39	3.58	374	1510	21	73	1978	1896	-	-	-	-	-	-
November	3	sfc	2.9	2.48	0.31	2.15	4.94	4.79	61	941	34	100	1121	1106	1.4	37.8	5.9	13.0	58.1	53.5
1975	3	8m	2.3	2.38	0.29	2.06	4.73	4.72	64	925	29	110	1128	1138	1.0	25.6	5.7	15.4	47.7	46.8
	Mean			2.37	0.28	1.96	4.61	4.50	118	1180	31	105	1428	1398	0.7	16.9	12.7	14.0	44.3	43.9
	(std. dev.)			±0.32	±0.05	±0.27	±0.54	±0.53	±105	±190	±5	±13	±266	±248	±0.4	±9.1	±3.8	±2.4	±6.2	±5.2
	% of total			51.4	6.1	42.5	100	-	8.2	82.3	2.2	7.3	100	-	1.6	38.1	28.7	31.6	100	-

(Note: all samples had < 2ppm Exch. Fe)

*Locations: 3 Head of Passes; 5 SW Pass; 6 So. Pass; see Fig. 5, p. 30.

Table 7 (continued)

Sampling period	Location	Water depth	Ni (ppm) Red.	Ox.	Res.	Total (sum)	Total	Pb (ppm) Red.	Ox.	Res.	Total (sum)	Total	Co (ppm) Red.	Ox.	Res.	Total (sum)	Total
	3	sfc	25.7	4.0	32.4	62.1	60.8	16.4	12.6	18.0	47.0	50.2	8.4	3.8	7.8	20.0	20.8
May-June	3	9m	25.4	7.9	29.6	62.9	62.0	18.0	28.0	15.3	61.3	56.6	8.7	-	8.3	-	21.6
1974	5	5m	25.3	2.5	33.6	61.4	59.6	18.7	-	-	-	62.4	-	-	-	-	19.1
	6	7m	24.0	3.6	30.2	57.8	57.5	14.7	15.5	17.0	47.2	41.0	9.3	1.5	9.3	20.1	-
Feb-Mar	3	sfc	18.5	5.7	31.6	55.8	54.0	15.5	-	15.8	-	40.3	8.4	-	9.9	-	18.8
1975	3	6m	22.5	2.5	29.8	54.8	57.4	16.3	10.3	16.9	43.5	42.8	8.4	1.5	8.5	18.4	18.8
July	3	sfc	19.8	1.4	28.3	49.5	52.0	20.1	14.6	13.8	48.5	47.7	9.9	3.0	8.0	20.9	22.2
1975	3	4m	21.0	4.8	26.7	52.5	51.3	17.4	12.7	14.9	45.0	49.2	8.0	11.7	6.2	25.9	24.8
September	3	sfc	24.9	0.7	19.1	44.7	45.5	23.5	-	10.6	-	42.4	8.3	5.0	7.0	20.3	18.1
1975	3	5m	28.9	<0.2	16.5	45.4	47.8	27.1	4.6	12.9	44.6	45.5	7.4	2.8	7.0	17.2	18.9
November	3	sfc	24.2	6.0	32.2	62.4	54.1	23.2	15.1	14.7	53.0	-	8.8	-	9.0	-	23.5
1975	3	8m	21.9	2.5	31.9	56.3	54.3	25.9	16.3	12.6	54.8	51.9	11.5	7.4	8.1	27.0	28.3
		Mean	23.5	3.5	28.5	55.5	54.7	20.3	14.4	14.8	49.4	48.2	8.8	4.6	8.1	21.2	21.4
		(std. dev.)	±2.9	±2.3	±5.4	±6.4	±5.1	±4.4	±6.2	±2.2	±5.8	±6.9	±1.1	±3.5	±1.1	±3.4	±3.2
		% of total	42.3	6.3	51.4	100	-	41.0	29.1	29.9	-	-	40.9	21.4	37.7	-	-

(Note: all samples had < 0.5 ppm Exch. Ni, Pb and Co)

fraction in Table 7) for the four normal sampling periods were 2.48 ± 0.22%. This is 51 ± 3% of the total particulate Fe present. For the September samples, the dithionite leachable Fe concentration was only 1.84%; yet this was a comparable 52% of the total Fe. A consistent 6.1 ± 0.7% of the total Fe was removed by oxidation with NaOCl although the absolute concentrations were 0.30 and 0.18% Fe for normal and low periods respectively. The exact nature of this Fe can not be specified, although it is unlikely that there is a sulfide fraction and thus part of the removed Fe may be associated with organic matter and part is from oxide material left after the $Na_2S_2O_4$ treatment. Lattice-held or residual Fe was 42 ± 2% of the total Fe present for all five periods. The September samples, however, had oxide phase and lattice-held Fe concentrations which were 25% lower than found for samples from the other periods. This decrease parallels the September total particulate Fe concentrations which also were 25% lower than normal. The mode of particulate Fe transport by the Mississippi River is thus remarkably uniform. This is a function of the uniform composition of the iron-bearing silicate material transported by the river as well as the uniform surface area and "free" iron available for coating mineral grains. Fe partitioning in the Mississippi particulates closely resembled partitioning found by GIBBS (1973) in Amazon and Yukon River particulates (Fig. 10).

In contrast to Fe, exchangeable Mn concentrations were very high in the river particulates with the highest values (300 and 374 ppm) measured during the low flow period. Easily exchangeable

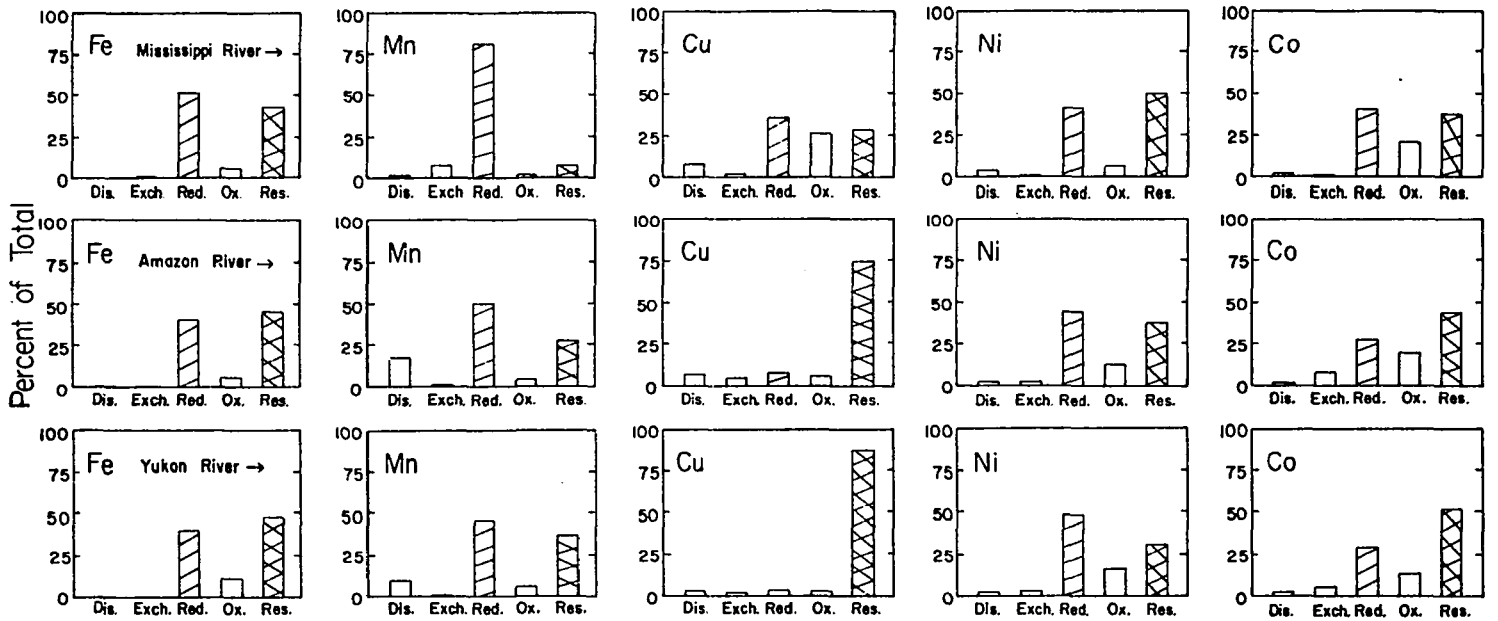


Fig. 10. Percentages of total Fe, Mn, Cu, Ni and Co transported by five phases in the Mississippi River (this study) and the Amazon and Yukon Rivers (GIBBS, 1973).

Mn (but not Fe) has also been removed from Pacific sediments (GOLDBERG and ARRHENIUS, 1958). This removal indicates that Mn may occupy exchangeable positions on clay surfaces. The increase in exchangeable Mn for the September period is probably related to the greater amount of higher surface area fine-grained material in the river at that time. This concept will be discussed further along with the data for the delta suspended matter. Reducible Mn concentrations were variable (925-1510 ppm), yet the percent of total Mn removed by the citrate-dithionite was a dominant 82 ± 4%. As in the case of Fe, the NaOCl removed a small (21 ppm Mn) but uniform (2.2 ± 0.5% of total) amount of Mn. During normal river flow, lattice Mn concentrations were 111 ± 5 ppm whereas at low flow they were only 79 ppm. This low flow value is about 71% of the 111 ppm normal value but is in good agreement with the 25% dilution of aluminosilicate material at low river stage. In summary, Mn is almost totally transported as a surface coated oxide with a significant exchangeable fraction and a small, consistent lattice component. These results are somewhat different from those of GIBBS (1973) who found only 50 and 46% of the total Mn as Mn oxides in the Amazon and Yukon suspended matter (Fig. 10). This difference may be due to lower total Mn concentrations in the particulates and/or the presence of a different suite of silicate minerals.

Mean values from Table 7 show that river particulate Cu is evenly distributed among the reducible, oxidizable and residual phases, even though there is some scatter from one sampling period

to another. Exchangeable Cu is quite low and quantitatively insignificant. Lattice-held Cu is a consistent 14 ± 2 ppm or 32 ± 6% of the total Cu. This percentage of total Cu removed is considerably lower than the 74 and 87% of total Cu removed by GIBBS (1973) from Amazon and Yukon River crystal phases (Fig. 10). Oxidizable Cu concentrations are also relatively uniform for the first three sampling periods (14 ± 1 ppm), however the November particulates had high total Cu concentrations (53 ppm) but only 6 ppm oxidizable Cu. Reducible Cu concentrations were a consistent 11 ± 1 ppm for the May-June and February-March particulates which averaged 40 ppm total Cu. However the reducible phase Cu was higher in the July (19 ppm) and November (32 ppm) samples and thus was responsible for increases in total concentrations to 48 and 53 ppm respectively. The September samples analyzed have been omitted from Table 7 because of apparent sample inhomogeneity which led to large variations in the replicate analyses of leachable as well as independent total Cu concentrations. Of particular interest are the concentrations of oxidizable phase Cu measured in these organic-rich samples (up to 73 ppm) a point to be discussed later in regard to the Gulf suspended matter. Cu, then, in sharp contrast to Mn or Fe, partitions between three of the phases identified and shows a greater tendency toward a significant metallo-organic association.

Forty-two percent of the particulate Ni is transported with "free" iron and manganese oxides and 51% of the particulate Ni is in silicate lattices. Oxide-phase Ni is a seasonally constant 24 ± 3 ppm, however the percentage of total Ni which this represents is

higher in the low river stage samples (57% at low flow vs. 40% at other times). Conversely, there is a decrease in lattice-held Ni from 31 ± 2 ppm during normal river flow to 18 ± 2 ppm in the atypical September period. This decrease (∿42%) is greater than that expected from the previously discussed 25% dilution of aluminosilicate detritus at low flow and may be related to a comparable decrease in silt-size particles (with associated minerals) since the high correlation (+0.93) of Ni with silt in river particulates suggests such a relationship. Exchangeable Ni concentrations were low (<0.5 ppm) and show that dissolved trace metals which are at ppb levels cannot compete well against the major cations for exchange positions. Oxidizable Ni concentrations were also low, averaging 4 ± 2 ppm for the four typical periods and <1 ppm for the low flow samples. These data downplay the importance of organic matter in Ni transport and are consistent with the lower total particulate Ni concentrations found during September. Particulate Ni partitioning in the Mississippi River is thus analagous to that of Fe with the bulk of each divided between oxide and lattice phases. Similar distribution of Fe and Ni was found in both the Amazon and Yukon Rivers (Fig. 10).

Lead, like Cu, is partitioned evenly among the reducible (40.1%), oxidizable (30.6%) and residual (29.2%) phases with exchangeable Pb <0.5 ppm. Lattice-held Pb is a consistent 15.4 ± 1.7 ppm for "average" river particulates and 23% less (11.8 ppm) in the lower aluminosilicate containing September samples. Oxide-phase Pb concentrations are also similar to those for Cu with the first two,

higher water flow sampling periods averaging 17 ± 2 ppm and the last three periods averaging 23 ± 4 ppm. Oxidizable Pb concentrations are more variable as determinations were subject to matrix interferences; yet in every instance there is a measurable and significant oxidizable fraction.

Cobalt partitioning appeared similar to that of Cu and Pb, even though its chemistry should perhaps be more comparable with that of Fe and Ni (GOLDSCHMIDT, 1958). Analytical difficulties with the oxidizable leach due to matrix interference may in fact have obscured its true behavior. Lattice-held Co was 8.3 ± 1.1 ppm for the normal periods and 7.0 ppm for the September samples which represents a uniform 38 ± 5% of the total. Reducible Co concentrations were also consistent at 8.8 ± 1.1 ppm and 41 ± 6% of the total. Oxidizable Co values were generally low with some anomalous values. Despite analytical problems, Co partitioning in Mississippi River particulates parallels that for the Amazon and Yukon (Fig. 10).

Chemical leaching of the Mississippi River suspended material has thus shown that particulate Fe and Ni are transported in oxide and lattice phases, that Mn is present predominantly as an oxide coating and that Cu, Pb and Co each have significant reducible, oxidizable and residual fractions (Fig. 10). Fe, Ni and Co partitioning in Mississippi River suspended matter are similar to partitioning found in samples from the Amazon and Yukon Rivers (Fig. 10) whereas Cu and Mn had a more significant lattice fraction in the Amazon and Yukon particulates than in those from the Mississippi. The present study also shows that lattice-held metal

concentrations are constant, yet sensitive to dilution by organic matter, a trend evident from the significant negative correlation between POC and lattice metal phases (Table 8). The correlation coefficient matrix also supports the existence of an Fe and Ni subgroup and the previously described differences in modes of particulate metal transport.

Comparison of Mississippi River data with data for one sampling period from other selected rivers (Table 9) re-emphasizes the sparsity of information on the metal content of river particulates and shows the variability among rivers. No metal data are accessible for some important Asian rivers (e.g. Yellow, Yangtze, Brahmaputra), yet HOLEMAN (1968) says Asian rivers account for 80% of river sediment flux to the oceans. Unfortunately, Amazon and Yukon River data (GIBBS, 1973) are only given as leachable percentages of the total for each metal. Values from the Susquehanna (CARPENTER et al., 1975) are variable enough to forestall the authors from estimating average concentrations. Nevertheless, many of the reported particulate metal concentrations (with the exception of Zn) approach average crustal abundances, a point to be considered in the following discussion.

Mississippi River particulate metal concentrations are compared with those for Mississippi drainage basin soils and average continental crust (Table 10) in order to contrast the composition of weathering products with parent material. Soil values in Table 10 are a compilation of Mississippi drainage basin surface soil data and, as could be expected, are subject to considerable variation.

Table 8. Correlation coefficients matrix for Mississippi River suspended matter metal partitioning data *

	Cl	TSM	POC	Fe Red.	Fe Ox.	Fe Lat.	Fe Sum	Mn Exch.	Mn Red.	Mn Lat.	Mn Sum	Cu Exch.	Cu Red.	Cu Ox.	Cu Sum	Ni Lat.	Ni Sum	Pb Red.	Pb Ox.	Pb Lat.
Cl	1.00																			
TSM	-0.75	1.00																		
POC	0.99	-0.73	1.00																	
Fe Red.	-0.80	-	-0.79	1.00																
Fe Ox.	-0.86	-	-0.86	-	1.00															
Fe Lat.	-0.75	-	-0.72	-	0.80	1.00														
Fe Sum	-0.94	-	-0.91	0.85	0.86	0.81	1.00													
Mn Exch.	0.96	-	0.92	-	-0.93	-0.88	-0.42	1.00												
Mn Red.	0.85	-	-	-	-	-	-0.67	0.76	1.00											
Mn Lat.	-0.95	-	-0.94	-	0.79	0.82	0.89	-0.91	-	1.00										
Mn Sum	0.94	-	0.74	-	-0.72	-0.73	-0.79	0.88	0.98	-0.77	1.00									
Cu Exch.	-	-	0.79	-	-	-	-	-	-	-	-	1.00								
Cu Red.	0.83	-	0.89	-	-	-	-	-	-	-	-	-	1.00							
Cu Ox.	-	-	-0.94	-	-	-	-	-	0.80	-	0.85	-	-0.85	1.00						
Cu Sum	0.85	-	-	-	-	-	-	-	-	-	-	-	0.92	-	1.00					
Ni Lat.	-0.94	-	-0.86	0.86	0.78	0.73	0.96	-0.89	-	0.86	-0.86	-	-	-	-	1.00				
Ni Sum	-0.78	-	-0.71	0.94	0.69	-	0.86	-0.67	-	-	-	-	-	-	-	0.86	1.00			
Pb Red.	0.91	-0.82	0.75	-	-	-	-	-	-	-	-	-	0.83	-0.87	-	-	-	1.00		
Pb Ox.	-	-	-	-	0.74	-	-	-	-	-	-	-	-	-	-	-	-	-	1.00	
Pb Lat.	-0.83	-	-0.77	0.85	-	-	0.71	-	-	-	-	-	-	-	-	-	0.69	-0.82	-	1.00

*Only correlations significant at $p<0.01$ are listed.

Table 9. Suspended sediment metal concentrations from selected rivers

	Fe (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)
SE U.S. Rivers (WINDOM et al., 1971)	5.37	750	660	-	115	29	380	180	-
Western U.S. Rivers	-	1020	-	-	-	19	92	44	-
Eastern U.S. Rivers	-	5700	-	-	-	41	230	150	-
Rhone River (TUREKIAN and SCOTT, 1967)	-	820	-	-	-	29	150	60	-
Amazon, Congo, Ganges, Mekong, Orinoco (CHESTER and ASTON, 1976)	4.38	700	310	187	226	16	100	65	-
Mississippi River (this study)	4.61	1300	193	46	45	21	79	55	1.3
Ave. continental crust (TAYLOR, 1964)	5.63	950	70	12.5	55	25	100	75	0.2
Ave. shale (TUREKIAN and WEDEPOHL, 1961)	4.72	850	95	20	45	19	90	68	0.3

HOLMES and HEARN (1942) and HOLMES (1943) analyses are for lower Mississippi alluvial soils and may be most comparable for the purpose of the table. Mississippi River suspended matter concentrations from this study are for all river samples including those from the low flow period. Because a disproportionate number of samples were collected and analyzed during normal and high periods, the averages in Table 10 are probably a close approximation of mean values. In fact, they are essentially the same as those for February-March and July 1975, the two most reliable and representative data sets. The U.S.G.S. (1975) data was calculated from river water "total" metal concentrations and despite the incredible range in concentrations (Table 10), their median values appear to be a useful indicator of the river particulate load.

The metal flux from the continents to the oceans is usually determined using average crustal abundances because of the unavailability of particulate metal data and because average abundance values smooth out geographical differences. This study shows, however, that Mississippi River particulate Fe, Cu, Cr, Co and Ni concentrations are about 20% below crustal averages, whereas Al and V are very close to crustal values and Mn is about 40% higher. These departures from crustal averages can be explained in part by the composition of parent material. Maximum soil Fe, Cu and Ni concentrations in the Mississippi drainage basin are also lower than crustal averages. Soil Mn values, however, have a reported 2200 ppm maximum and average 800 ppm (Table 10). Average river particulate Mn concentrations (1300 ppm) are higher than soil values

Table 10. Metal concentrations in Mississippi River drainage basin soils, Mississippi River particulates and continental crust

		Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	As (ppm)
Mississippi River drainage basin soils	Mean	2.86[a]	6.57[a]	800[a]	94[a,b]	22[c]	23[b]	8[c,d]	50[c,d]	14[c]	< 1[c]	84[c,d]	8[c,d]
	Range	4.50 to 1.28	9.92 to 4.02	2200 to 100	167 to 50	150 to 10	34 to 13	30 to 2	150 to 10	70 to <5	-	200 to 15	17 to 1
Mississippi subaerial delta (this study)	(N=13)	3.10	6.63	630	-	26	24	18	62	29	0.5	100	7
Mississippi River bed - SW Pass (this study)	(N= 1)	1.91	5.28	460	61	21	15	17	54	23	-	-	-
Mississippi River suspended particulates* (U.S.G.S., 1975)	Median (N=87)	2.00	-	1100	233	49	28	14	58	-	3	-	14
	Range	5.45 to 0.26	-	3790 to 395	9000 to 12	1143 to 9	119 to 15	48 to 11	364 to 33	-	690 to 2	-	400 to 2
Mississippi River suspended particulates (TUREKIAN and SCOTT, 1967)	(N= 1)	-	-	2300	-	-	-	33	150	100	-	-	-
Mississippi River suspended particulates (this study)	Mean (N=43)	4.57	8.63	1300	196	45.8	45.5	20.3	80	55.4	1.3	150	14.6
	Range	5.13 to 3.30	9.39 to 6.24	1900 to 1110	256 to 152	62.4 to 35.0	61.6 to 35.6	24.8 to 18.1	-	62.7 to 45.4	2.4 to 0.8	-	-
Continental crust		5.63	8.23	950	70	12.5	55	25	100	75	0.2	135	1.8

[a] HOLMES and HEARN (1942), N=29.
[b] HOLMES (1943), N=23.
[c] CONNOR and SHACKLETTE (1975).
[d] SWAINE (1955).

* Values calculated from U.S.G.S. "total" river metal concentrations by [("total" in µg/ℓ - dissolved in µg/ℓ) ÷ suspended sediment in g/ℓ].

and suggest that preferential chemical and physical weathering have favored Mn removal to the river load.

In sharp contrast to the above elements, Zn, Pb, Cd and As concentrations are several times higher in river particulates than in average crustal material. Mississippi Delta sediments have been shown to have a significant anthropogenic contribution of Pb and Cd (TREFRY and PRESLEY, 1976a) and the average soil values for each of the above metals is higher than the crustal average, especially so in the case of As and Pb. Although some of the soil values may be related to cultivation and fertilization, high values are also found in uncultivated areas (CONNOR and SHACKLETTE, 1975). It appears, then, that Zn, Pb, Cd and As concentrations are high due to the mineralogy of the drainage basin and/or anthropogenic inputs.

Table 10 shows that Mississippi River drainage basin soils have lower average metal levels than river particulates and that the soils are more comparable to Mississippi subaerial delta sediments. River bed sediments, however, have the lowest metal concentrations in most cases. These differences correlate well with grain-size distribution according to the data in Table 11.

A plot of percent clay versus Fe content (Fig. 11) for the above data illustrates this relationship. Fig. 11 also shows that clay-free soil or sediment will have low Fe concentrations (1.0-1.5%) and that clay-rich samples may have 4-5 times greater Fe content.

The major element chemistry of the Mississippi River particulates also has been determined and is compared with crustal abundance

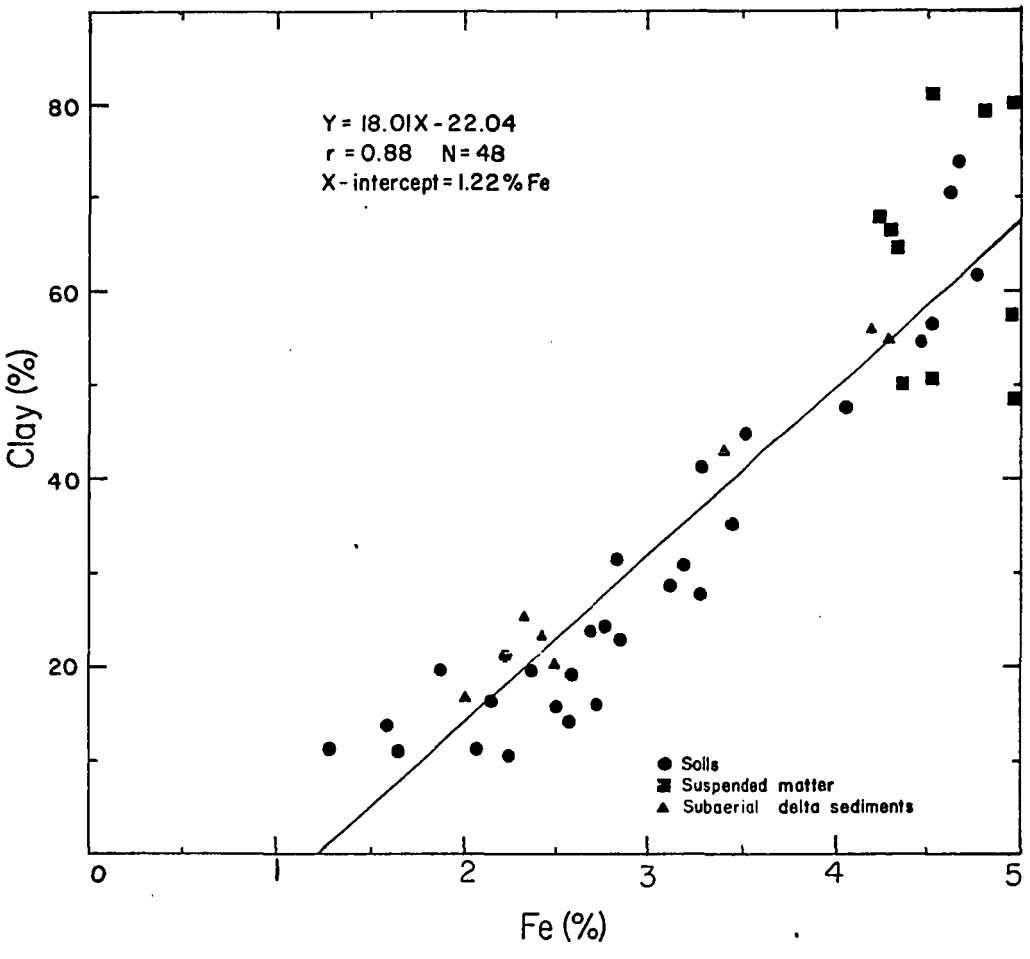


Fig. 11. Clay vs. Fe scatter plot for Mississippi River drainage basin soils (data from HOLMES and HEARN, 1942) and Mississippi River suspended matter and subaerial delta sediments.

Table 11. Grain size distribution and metal concentrations in Mississippi Delta soils and Mississippi River sediments and suspended matter

	Sand (%)	Silt (%)	Clay (%)	Fe (%)	Cu (ppm)	Mn (ppm)
Mississippi soils*	16	54	30	2.86	23	800
Mississippi subaerial delta sediment	6	60	34	3.10	24	630
Mississippi River bed sediments	36	42	22	1.91	15	460
Mississippi River particulates	0.2	41.1	58.7	4.57	46	1300

*HOLMES and HEARN (1942), sand-silt boundary used was 50 μm.

data in Table 12. SiO_2, Al_2O_3, Fe_2O_3 and K_2O concentrations in Mississippi suspended matter are similar to crustal values and to Mississippi sediment data. Na_2O, CaO and MgO values, however, are 60-86% below crustal abundances. These trends are reversed in river dissolved concentrations (Table 13). Dissolved Mg, Ca and Na concentrations in the Mississippi River (Table 13) are about three times greater than average river water. Potassium concentrations in the Mississippi are equivalent to those for average river water and dissolved Si and Fe concentrations are considerably lower. The lower particulate Mg, Ca and K concentrations observed in the Mississippi River may be due to greater than normal chemical weathering and dissolved transport of these elements. Comparison of average river major element loads with those for the Mississippi River (Table 13) show, in fact, that the Mississippi has a somewhat

Table 12. Major element composition of Mississippi River suspended and bottom sediment, deep-sea clay and continental crust (concentrations in weight %)

	Mississippi River Suspended Sediment (this study)	Mississippi River Sediment (HOLMES and HEARN, 1942)	Mississippi Silt (CLARKE and STEIGER, 1914)	Deep Sea Clay (EL WAKEEL and RILEY, 1961)	Continental Crustal Ave. (TAYLOR, 1964)
SiO_2	61.94	62.96	69.96	55.34	60.24
Al_2O_3	16.37	16.30	10.52	17.48	15.55
Fe_2O_3	6.58	6.10	3.47	8.23	7.77
K_2O	2.26	2.79	2.30	3.26	2.51
MgO	1.66	2.40	1.41	4.25*	3.87
CaO	1.51	2.55	2.17	1.72*	5.81
Na_2O	0.62	2.39	1.51	1.53	3.19
TiO_2	0.71	0.71	0.54	0.84	0.76
Organic matter	(1.1)†	1.88	2.06	0.24†	-
H_2O	-	2.62	5.74	6.54	-
Ignition loss (600°C)	6.95	(5.91)	-	-	-
Total	98.60	100.7	99.68	99.43	99.7

* Includes $MgCO_3$ and $CaCO_3$ respectively. † Organic carbon.

Table 13. Major element loads for average river water and the Mississippi River

Element	Continental Crust[1] (mg/g)	Average river water[2] (mg/ℓ)	Total* (mg/ℓ)	Miss. River susp. matter[3] (mg/g)	Miss. River dissolved[3] (mg/ℓ)	Total* (mg/ℓ)
Mg	23.3	4.1	16	10.0	12	17
Ca	41.5	15	36	10.8	40	45
Na	23.7	6.3	18	4.6	21	23
K	20.8	2.3	13	18.8	3	12
Fe	54.3	0.7	28	46.0	0.01	23
Al	82.3	-	41	86.6	-	43
Si	282	6.2	147	290	3.1	148

* Totals calculated by multiplying solids concentrations (mg/g) by average river particulate load (0.5 g/ℓ) and adding dissolved load.

1 TAYLOR (1964).

2 LIVINGSTONE (1963).

3 This study.

higher total burden of Mg, Ca and Na than the average river and a similar total load of K, Al and Si.

River Dissolved Trace Metals

Dissolved trace metal concentrations in Mississippi River water have been measured with some regularity in recent years, the U.S. Geological Survey spearheading a large analytical program. Considerable variation in reported results is found (Table 14). This may be partially explained by differences in filter pore size. For example, DURUM and HAFFTY (1961) used 2 µm glass fiber filters whereas most other investigators used 0.45 or 0.4 µm membrane filters. Differences in analytical techniques, sampling apparatus and storage containers also contribute to the observed variability in metal values.

Concentrations in the few samples analyzed for this study are somewhat lower than those previously reported (Table 14). However many investigators (Table 14) have found concentrations of some elements below their detection limits a large percentage of the time. Cr and Cd concentrations, for example, are consistently below the reported 1 µg/ℓ detection limits reported by the U.S.G.S. Average Cr and Cd values determined in this study (0.6 and 0.15 µg/ℓ respectively) confirm the suggested low concentrations. Although Cu and Ni analyses for the Mississippi have been made less frequently the results of this study and that of the U.S.G.S (1975) for South-west Pass agree quite well (Table 14). Mississippi River Mn and Fe concentrations are lower than frequently reported for other rivers,

Table 14. Mississippi River dissolved trace metal concentrations

Location	Kilometers above Head of Passes	No. of Samples		Fe (µg/l)	Mn (µg/l)	Pb (µg/l)	Cu (µg/l)	Ni (µg/l)	Cr (µg/l)	Cd (µg/l)	Zn (µg/l)	Hg (µg/l)	As (µg/l)
Baton Rouge (DURUM and HAFFTY, 1961)	380	4		1050	81	6	10	16	5	-	-	-	-
New Orleans (KOPP and KRONER, 1967)	166	18	Mean % Frequency of detection*	22 (72.2)	3.6 (38.9)	54 (22.2)	9 (77.8)	- -	8 (22.2)	- (0.0)	23 (66.7)	- -	- -
Baton Rouge (DAVIS, 1968)	380	1		-	11	2.5	0.9	0.5	-	-	-	-	-
New Orleans (DURUM et al., 1970)	166	2		-	-	< 1	-	-	< 1	6	< 1	< 0.5	-
St. Francisville to Venice (U.S.G.S., 1972, 1973, 1974)	430 to 18	486	Mean % Frequency of detection**	35 (71.5)	- -	5 (39.3)	8† (21.2)	- -	2 (< 1.0)	2.5 (30.1)	23 (69.9)	0.4 (24.5)	3 (38.1)
St. Francisville to Venice (U.S.G.S., 1975)	430 to 18	87	Mean % Frequency of detection**	35 (67.3)	27 (35.3)	2 (63.4)	5† (100)	-	3 (10.5)	1 (19.7)	16 (82.9)	0.1 (51.3)	1 (79.0)
Southwest Pass (U.S.G.S., 1975)	0 to -35	7		-	-	< 1	3	3	< 1	< 1	10	< 0.1	3
Head of Passes (This study, 1974, 1975)	0	10		5	10	< 1	2	1.5	0.5	0.1	-	-	-
Average River Water (TUREKIAN, 1969)	-	-		-	7	3	7	0.3	1	-	20	0.07	2

* Lowest detected values were 5 µg/l for Zn and Cr, 8 µg/l for Fe, 2 µg/l for Cu, 28 µg/l for Pb, and 0.6 µg/l for Mn.

** Detection limits given as 0.5 µg/l for Hg, 1.0 µg/l for Cd, Cr, Co and Pb, 10 µg/l for Zn and As, however, for some analyses detection limits were higher.

† Analyses given for only a few samples.

yet Mississippi investigators (Table 14) have consistently found 5-35 µg/ℓ for each. Pb concentrations determined in this study by solvent-extraction (0.2- 0.3 µg Pb/ℓ) and direct injection into an atomic absorption spectrophotometer (∿1 µg/ℓ) were in disagreement. This difference may be due to the form of the dissolved Pb and thus all one may say is that average Pb concentrations are certainly <1 µg/ℓ.

In general, Mississippi River dissolved metal concentrations are equal to or lower than those given for average river water (TUREKIAN, 1969). These low concentrations are probably controlled by adsorptive processes since the abundant fine-grained material and high river pH (7.5-8.1) favor such processes.

Seasonal variability in dissolved metal concentrations make it difficult to assess the river dissolved metal flux. CARPENTER, et al. (1975) found Susquehanna River dissolved Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn concentrations to be highest during peak water and suspended solids discharge and low during low water and suspended solids discharge. Concentrations varied by factors of from 4 to >100.

Spatial and temporal variability was also examined in the 569 Mississippi River samples analyzed by the U.S.G.S. from 1972-1975. These samples were collected by the U.S.G.S. at seven locations along the lower Mississippi River from St. Francisville, Louisiana (430 km above Head of Passes), to Venice, Louisiana (18 km above Head of Passes). Chloride ion concentrations (Fig. 9) show seasonal ranges of 12 to >50 mg/ℓ and are inversely related to water flow.

Specific conductance and other major elements behave similarly. Percent frequencies of detection and average metal concentrations were quite uniform along the 412 km stretch of the lower Mississippi and thus the data was reduced to a single entry in Table 14. Furthermore, there was no obvious, consistent relationship between the values found by the U.S.G.S. or the frequency of finding detectable amounts, and time of year, river flow, suspended load or other such variables. Dissolved trace metal analyses from my study were few in number, however, no significant seasonal changes in concentration were observed. This is consistent with the results of the U.S.G.S. (1972-1975).

Annual Metal Flux from the Mississippi River to the Gulf of Mexico

To calculate the total flux of dissolved and particulate trace metals from the Mississippi River to the Gulf of Mexico it is necessary to know the water and sediment load of the river as well as the metal concentrations in each. Best estimates of particulate and dissolved metal levels in the Mississippi River are given in Tables 10 and 14 respectively. A brief background pertinent to the choice of water and sediment load values follows below.

Mississippi River sediment and water discharge have been monitored intermittently since 1851, however it was not until 1950 that the U.S. Army Corps of Engineers established a comprehensive sediment and water sampling program. CURTIS et al. (1973) note that suspended-sediment discharge recorded from 1851-1931 was 30% higher than during the period 1950-1969, yet much of this decrease appears

to have occurred during the early 1950's. A comparison of sediment and water discharge for the period 1950-1952 with 1973-1975 (Fig. 12) shows, for example, that water flow was higher during the 1970's period whereas the sediment flux was 2.5 times lower. This decrease, which is related to upstream damming, certainly brings with it a corresponding recent decrease in sediment transported to the Gulf of Mexico. The picture is further complicated by the diversion of ∿30% of the Mississippi flow to the Atchafalaya River and the present-day deposition of the Atchafalaya sediment flow primarily in Atchafalaya Bay. Despite these changes, particularly the reduction of sediment transport directly to the Gulf, published water flow (5.7×10^{14} ℓ/y; ISERI and LANGBEIN, 1974) and sediment load (2.8×10^{14} g/y, U.S. ARMY CORPS OF ENGINEERS, 1950-1974) values are most representative of river discharge over the past 25 years. These values may also be representative of river discharge during the past several hundred years.

Particulates transport most of Mississippi River metal load to the Gulf of Mexico (Table 15). Although this river metal flux is small on a global scale (probably <3%, HOLEMAN, 1968) it accounts for at least 75% of the metal flux to the Gulf of Mexico (MOODY, 1967). The particulate load given in Table 15 does not include bed load, however bed loads have been estimated to be <10-20% of suspended loads (HOLLE, 1952; FISK et al., 1954). Since Mississippi River bed sediments have much lower metal content than the particulates (Table 10) they probably make up <10% of the annual flux. As expected, only a small percentage of all metals are

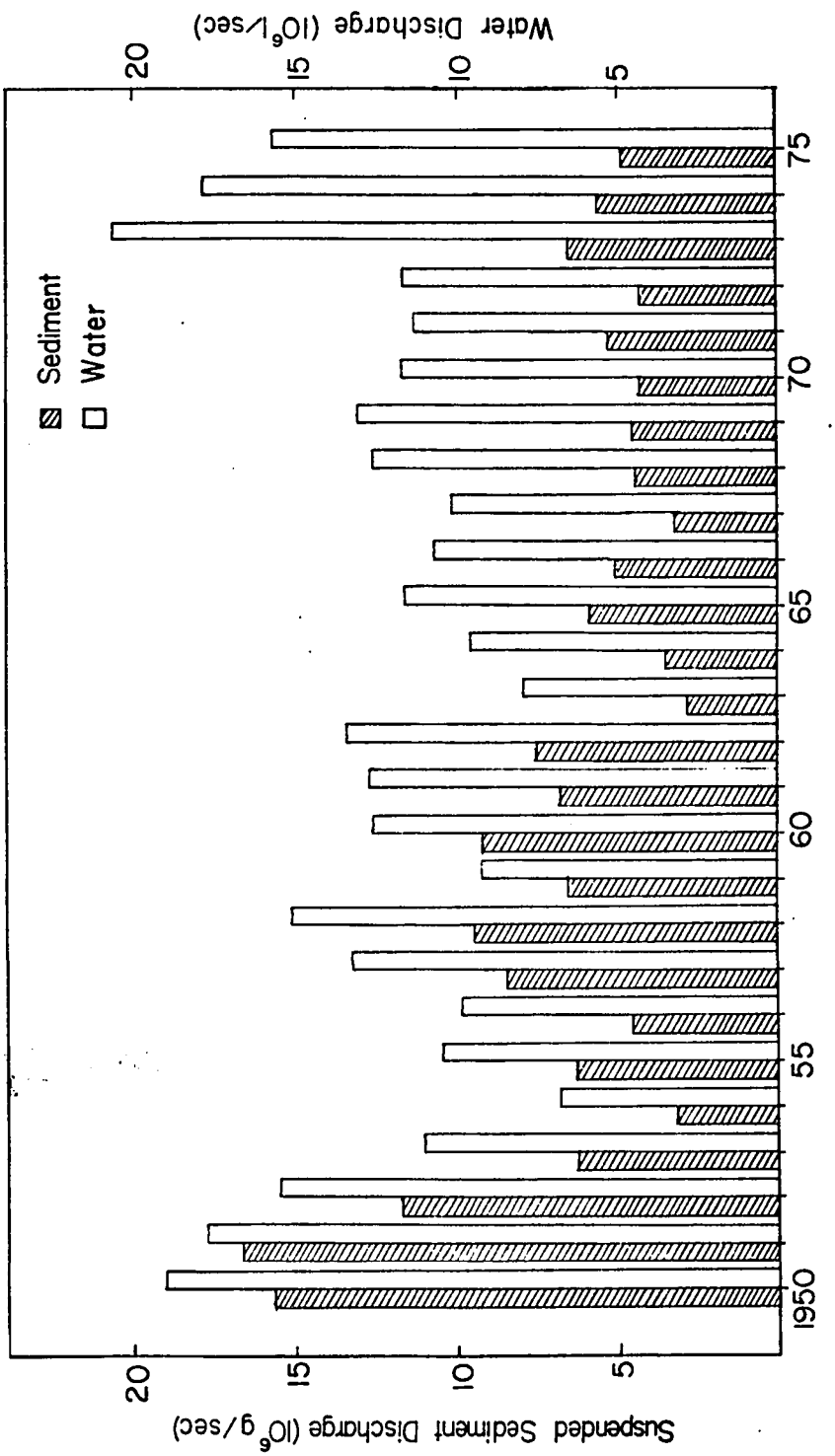


Fig. 12. Mississippi River average suspended sediment and water discharge for 1950-1975 (data from U.S. ARMY CORPS OF ENGINEERS, 1950-1975).

Table 15. Annual flux of metals from the Mississippi River to the Gulf of Mexico

Element	Particulate (x 10^9g)	Dissolved (x 10^9g)	Particulate (% of total)	Dissolved (% of total)
Fe	12,900	5.7	>99.9	0.02
Mn	364	5.7	98.5	1.5
Zn	54	5.7	90.4	9.6
Cr	22	0.3	98.7	1.3
Ni	16	0.6	96.4	3.6
Cu	13	1.1	92.2	7.8
Pb	13	0.3	97.7	2.3
As	4	0.6	87.0	13.0
Cd	0.4	0.06	87.0	13.0

NOTE: Calculations are based on average water and suspended matter metal data from Tables 10 and 14 with the sediment discharge data of the U.S. ARMY CORPS OF ENGINEERS (2.8 x 10^{14}g/y; 1950-1974) and estimated water flow at the river mouths (5.7 x 10^{14}ℓ/y; ISERI and LANGBEIN, 1974).

carried in solution and thus the primary modes of metal transport by the Mississippi are the "free" oxide and crystal lattice phases of the river particulates.

Mississippi Delta Suspended Matter

Metal concentrations in suspended material from Gulf of Mexico waters immediately outside the Mississippi River mouth were generally more variable than those from within the river (Table 16). The larger standard deviations for delta samples may be prompted by more widely varying chlorinity (0.2-20.0%), POC (0.07-1.66 mg/ℓ), TSM (1.8-65.0 mg/ℓ), POC/TSM (0.75-18.0%), DOC (0.79-4.94 mg/ℓ), pH (7.86-8.57) and dissolved silica (2.5-110 µM) in Mississippi Delta waters than in the river. However, average particulate Fe, Al, Mn, Co, Cr, Ni and Cd values for all samples from all seasons were essentially the same inside and outside the river. Zinc, Pb and Cu values were 25% higher in Gulf particulates (Table 16). Where there are differences in particulate metal concentrations between the two environments, they would probably be brought about by the higher POC/TSM values in the delta particulates (ave. 4.6%, with a maximum of 18% vs. <2% for the river) and the higher percentage of fine-grained particles in delta suspended matter (78% <2 µm vs. 58% in the river).

Observed high Cu concentrations in nearshore Gulf of Mexico suspended matter may be due to biological or organic matter enrichment of Cu. For example, one surface particulate sample collected (July 1975, Station 9) contained a large copepod larva and had a Cu

Table 16. Mississippi River Delta suspended sediment metal concentrations

Cruise	No. of Samples	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	POC/TSM (%)	TSM (mg/ℓ)	Silt (%)	Clay (%)
74-G-9															
29 May - 2 June 1974	6	4.82 (±0.23)	8.90 (±0.90)	1320 (±160)	224 (±12)	61.2 (±14.9)	48.6 (±4.4)	19.0 (±2.3)	-	63.5 (±10.5)	1.7 (±0.3)	0.9 (±0.2)	40 (-)	19.6 (±1.1)	80.4 (±1.1)
75-G-1															
26 Feb. - 1 Mar. 1975	6	5.19 (±0.64)	9.42 (±0.64)	1000 (±160)	217 (±25)	74.2 (±19.7)	66.6 (±12.4)	19.8 (±1.7)	-	61.4 (±5.8)	1.4 (±0.5)	2.2 (±1.2)	26 (-)	-	-
75-G-8															
10-14 July 1975	12	4.67 (±0.36)	9.10 (±0.73)	1200 (±130)	230 (±22)	46.6 (±4.2)	49.0 (±4.2)	22.1 (±2.2)	84 (±11)	53.5 (±4.1)	1.5 (±0.6)	1.5 (±0.9)	20 (±10)	24.2 (±7.0)	75.6 (±7.0)
75-G-11															
7-9 September 1975	6	4.03 (±0.68)	7.51 (±1.00)	1620 (±550)	230 (±65)	52.4 (±4.3)	51.7 (±5.5)	22.6 (±4.6)	-	51.6 (±3.7)	1.6 (-)	9 (±4)	9.6 (±5.4)	-	-
75-G-16															
16-17 November 1975	4	4.28 (±0.42)	8.33 (±0.65)	1290 (± 40)	288 (±81)	64.3 (±18.7)	64.6 (±3.6)	20.0 (-)	-	54.4 (±9.9)	1.6 (-)	11 (-)	9.7 (±6.9)	-	-
Mississippi River delta particulates															
Mean (std. dev.)	34	4.64 (±0.58)	8.78 (±0.98)	1230 (±220)	244 (±52)	58 (±16)	56 (±13)	21 (±2)	84 (±11)	56 (±8)	1.5 (±0.6)	4.6 (-)	30 (-)	21.8 (±4.9)	78.0 (±5.0)
Mississippi River particulates															
Mean (std. dev.)	43	4.61 (±0.40)	8.65 (±0.70)	1300 (±180)	193 (±29)	46 (±6)	45 (±7)	21 (±2)	79 (±3)	55 (±4)	1.3 (±0.4)	<2.0 (-)	149 (±105)	40.8 (±8.7)	59.0 (±8.7)

Note: Complete Delta suspended matter data set is given in APPENDIX D. Sample locations 7,8 and 9; Fig. 5, p. 30.

concentration of 171 ppm. The concentrations of other metals in this sample were not abnormal. Several other high Cu values (96, 86, 76 and 74 ppm) were also measured in Gulf particulates. Deleting these from the remaining 28 values reduces the mean Cu values only slightly (56 to 53 ppm). Considering the higher percent organic carbon in the Gulf particulates (5% vs. <2% for the river) and the significant correlation of Cu with organic C, biological and/or organic enrichment best explains the observed 25% higher Gulf Cu values.

Lead concentrations in river-mouth particulates group into a set of 24 samples with 35-58 ppm ($\bar{x}$ = 49) and a set of 10 with 69-94 ppm ($\bar{x}$ = 80). All three Gulf samples collected in Niskin bottles and filtered on ship during the May-June 1974 period were high in Pb ($\bar{x}$ = 74 ppm), but not in Fe ($\bar{x}$ = 4.72) or other metals. Samples from the same locations collected in plastic carboys and filtered later had normal Pb ($\bar{x}$ = 48), Fe ($\bar{x}$ = 4.92), and other metal values. Thus, it appears that contamination was a possible problem in low TSM samples from the initial field effort. Of the remaining seven high Pb values, five were from samples with <20mg TSM/ℓ. Yet, eight other <20 mg TSM/ℓ samples had "average" Pb concentrations. Only three of the nineteen delta particulate samples from >20 mg TSM/ℓ water seem anomalous. There does not appear to be any simple relationship between the high Pb values and another parameter such as the organic matter/Cu association, and thus random contamination is a plausible cause of the high Pb values.

Assuming the river particulate Pb average (46 ppm) to be

reasonable since nearshore surface sediments average 44 ppm, it appears that there is Pb contamination in the "high" Pb samples. If this contamination were as large as 1 µg Pb/ℓ, then samples with only 20 mg TSM/ℓ would contain 95 µg Pb/g (the observed maximum) rather than the expected 44 µg Pb/g. Similar contamination in a sample with 200 mg TSM/ℓ would only increase the concentration to 50 µg Pb/g. Clearly, many samples do not have any detectable contamination, however, the preceding discussion reemphasizes the potential dangers of Pb contamination, even at µg levels. Until further work shows differently, the high Pb values will be attributed to contamination and the 49 ppm average for the more normal delta samples will be accepted. This means that no significant change in particulate Pb values occurs between the river and delta.

Higher delta particulate Zn concentrations (26% higher than river particulates) are less easily explained than the Cu or even the Pb deviations. For example, Niskin sample values (196 ± 28 ppm Zn; N = 5) compare well with carboy sample concentrations (201 ± 28 ppm Zn; N = 5). Yet Zn values in both cases are high relative to shale (95 ppm), delta sediments (133 ppm) or deep-sea clay (165 ppm). If the Zn values are real then it suggests a high burden of anthropogenic Zn or high Mississippi River drainage basin values.

Mississippi Delta particulates were analyzed to determine whether any physico-chemical alterations involving heavy metals occur across the freshwater-seawater interface. Such reactions may alter the composition of the sediment and the ultimate area of metal deposition. For example, desorption of metals from river

particulates would delay metal removal to the sediments and promote an increased metal flux to deep water whereas adsorption of river dissolved metals on river particulates would have an opposite effect. Measuring particulate metal concentrations across the freshwater-seawater interface is a less sensitive means for detecting chemical changes than analyzing the dissolved fraction. However, particulates will identify any significant desorption and may be less prone to previously described interpretational problems.

Mississippi River particulate metal concentrations are similar to those for the delta (Table 16 and Fig. 13). This uniformity across the freshwater-seawater interface does not support extensive desorption of any of the metals studied. Iron, Al, Mn, Co, Cr, Ni, Cd and Pb concentrations are essentially the same in both Mississippi River and Mississippi Delta suspended matter. Cu (and perhaps Zn) increase across the interface, apparently related to an increase in organic matter. These observations are consistent with the laboratory and field studies of JOHNSON et al. (1967), MURRAY and MURRAY (1973) and O'CONNOR and KESTER (1975) which show that at the pH's of the river ($\sim$8.0) and the delta ($\sim$8.4) water there should be no significant sorptive reactions involving Cu, Co, Zn, or Cr.

Metal partitioning in Mississippi Delta suspended matter (Table 17) is generally similar to that found for river particulates. Reducible and lattice-held phases are quantitatively most important. Metal concentrations in the delta samples used for leaching are representative of metal concentrations for the entire data set (Table 16) and also reflect seasonal differences.

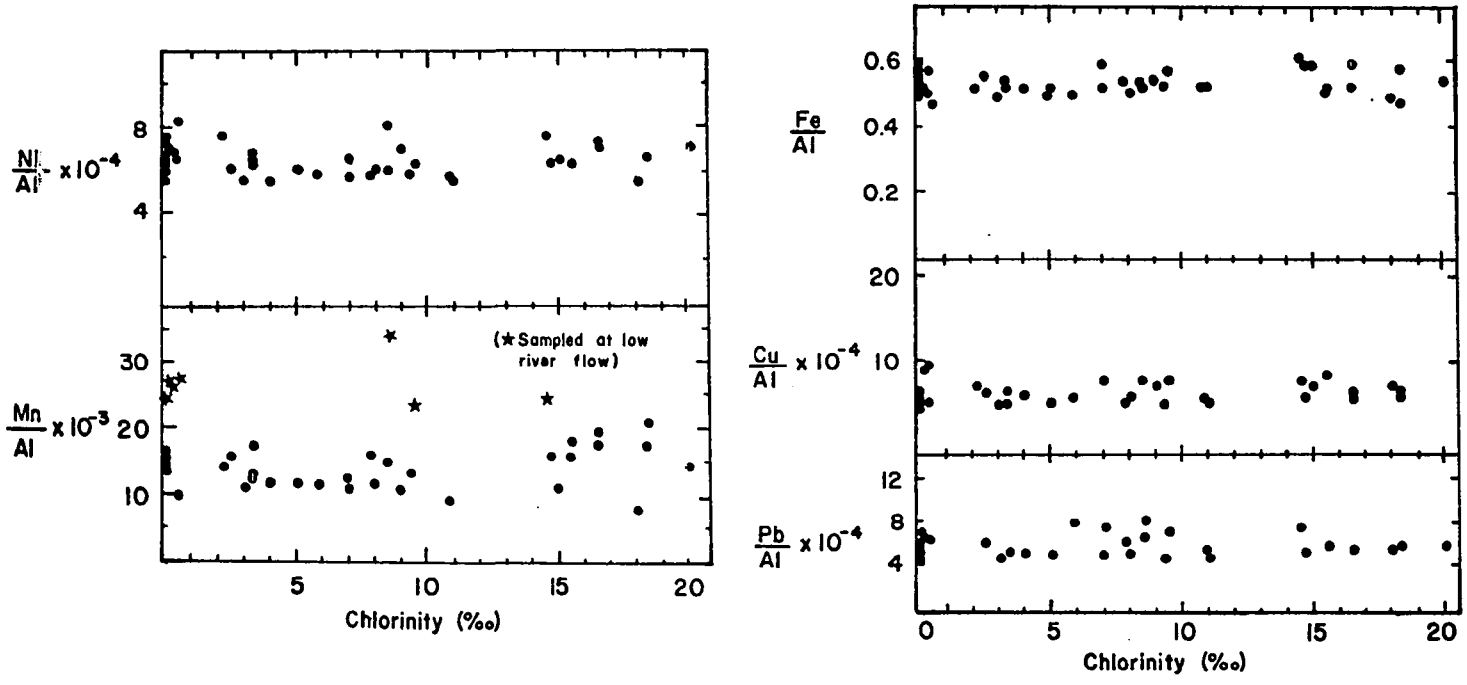


Fig. 13. Particulate metal/Al values across the Mississippi Delta freshwater-seawater interface.

Table 17. Chemical partitioning of metals in Mississippi Delta particulates

Sampling period	Location*	Water depth	Cl (°/₀₀)	POC/TSM (%)	Fe (%) Red.	Ox.	Res.	Total (sum)	Total	Mn (ppm) Exch.	Red.	Ox.	Res.	Total (sum)	Total	Cu (ppm) Exch.	Red.	Ox.	Res.	Total (sum)	Total
Feb-Mar 1975	9	sfc	0.25	1.5	3.24	0.30	2.25	5.79	5.83	103	774	22	105	1004	1006	0.5	25.4	8.7	14.0	48.6	48.9
	7	12m	18	1.2	2.06	0.24	2.06	4.36	4.36	79	520	18	94	711	708	0.7	30.9	6.5	20.0	58.1	61.4
	5	14m	6	0.6	2.08	0.28	2.13	4.49	4.49	53	940	28	101	1122	1073	1.4	22.9	7.4	18.5	50.2	51.7
	8	sfc	3	1.0	2.10	0.26	2.07	4.43	4.61	72	815	28	110	1025	1048	1.2	14.9	6.1	22.6	44.8	46.6
	7	sfc	3-4	1.2	2.14	0.33	2.04	4.51	5.01	91	931	32	101	1155	1155	1.3	18.7	10.3	12.9	43.2	51.7
	9	sfc	3,7	1.8	2.12	0.27	2.13	4.52	4.13	111	1025	28	115	1279	1226	3.6	37.0	29.2	11.1	80.9	75.6
July 1975	8	sfc	7-9	-	2.11	0.27	2.09	4.47	4.60	110	787	23	114	1034	1029	1.5	18.6	17.3	12.1	49.5	53.2
	7	sfc	9-10	-	2.29	0.27	2.30	4.86	5.09	118	1072	34	120	1344	1287	0.7	22.4	3.6	18.1	44.8	47.7
	9	sfc	16-18	-	-	0.32	1.91	-	-	209	1209	38	106	1562	-	(11)	(38)	(40)	(18)	(107)	-
	8	4m	18	0.8	2.13	0.27	2.16	4.56	4.36	171	1169	36	114	1490	1378	1.6	18.9	9.8	12.0	42.3	44.6
	7	-	17-19	3.3	2.08	0.38	1.91	4.37	4.22	360	1304	37	104	1805	1838	3.4	25.8	17.2	10.3	56.7	55.4
	5	12m	10.8	2.9	2.15	0.35	1.97	4.47	4.45	239	480	25	111	855	788	1.0	17.2	18.1	12.7	49.0	46.3
September 1975	6	-	-	-	1.91	0.15	1.52	3.58	-	-	-	-	-	-	-	(3)	(50)	(38)	(12)	(103)	-
	8	sfc	8-11	-	2.16	0.33	2.11	4.60	4.57	314	1397	38	98	1847	1864	3.3	17.4	20.9	17.5	59.1	59.0
	8	5m	14-15	10.9	2.05	0.19	1.06	3.30	-	-	-	-	-	-	-	2.8	22.2	16.2	11.2	52.4	51.3
	9	sfc	2.1	6.5	2.36	0.43	2.21	5.00	4.68	115	967	46	106	1234	1241	2.4	28.6	12.1	14.4	57.5	64.0
November 1975	8	sfc	7-10	-	2.21	0.36	1.93	4.50	4.46	224	957	39	102	1322	1271	3.3	23.9	19.2	15.5	61.9	64.5
	9	6m	15-16	14.1	2.31	0.36	1.26	3.93	4.28	308	897	33	80	1318	1308	6.9	51.3	7.9	8.1	74.2	69.5
	8	9m	14-17	18.0	1.77	0.30	1.56	3.63	3.70	263	912	37	99	1311	1339	-	-	-	-	-	-
		Mean			2.21	0.31	2.01	4.53	4.55	173	950	32	105	1260	1240	2.2	24.8	13.2	14.4	54.6	55.7
		(std. dev.)			±0.31	±0.05	±0.26	±0.46	±0.47	±96	±243	±7	±9	±303	±310	±1.6	±9.1	±6.9	±3.9	±10.8	±9.1
		% of total			48.8	6.8	44.4	100	-	13.7	75.4	2.6	8.3	100	-	4.0	45.4	24.2	26.4	100	-

(Note: all samples had < 2ppm Exch. Fe)

*Locations: 5 SW Pass; 6 So. Pass; 7 outside plume-outside SW Pass; 8 In-plume-outside SW Pass; 9 outside So. Pass; See Fig. 5, p. 30.

Table 17 (continued)

Sampling period	Location	Water depth	Ni (ppm) Red.	Ox.	Res.	Total (sum)	Total	Pb (ppm) Red.	Ox.	Res.	Total (sum)	Total	Co (ppm) Red.	Ox.	Res.	Total (sum)	Total
Feb-Mar 1975	9	sfc	25.3	2.2	36.4	63.9	66.7	53.0	10.4	24.6	88.0	88.4	-	2.1	8.9	-	20.7
	7	12m	22.0	2.2	30.1	54.3	50.7	23.7	15.0	11.6	50.3	49.8	-	5.1	8.4	-	16.8
	5	14m	17.6	2.6	29.9	50.1	50.4	30.9	23.4	17.7	72.0	72.2	7.4	-	9.3	-	22.4
	8	sfc	19.2	1.9	31.1	52.2	52.1	15.2	14.7	16.0	45.9	43.7	6.3	4.2	9.0	19.5	21.8
	7	sfc	17.1	7.8	31.7	56.6	52.2	16.8	20.0	12.2	49.0	49.4	6.8	4.6	9.3	20.7	22.0
July 1975	9	sfc	20.7	3.4	27.0	51.1	46.5	21.0	10.6	14.0	45.6	43.0	6.9	-	6.8	-	19.4
	8	sfc	21.6	1.3	27.7	52.0	54.5	16.9	12.1	15.7	44.7	43.8	8.4	2.2	8.8	19.4	-
	7	sfc	18.3	1.3	33.5	53.1	56.9	21.8	-	18.9	-	44.2	8.0	4.7	9.1	21.8	23.0
	9	sfc	18.0	4.9	27.8	50.7	-	20.4	38.8	14.8	74.0	76.3	6.9	-	7.7	-	25.0
	8	4m	18.8	1.0	29.5	49.3	52.4	21.2	-	22.3	-	45.1	7.5	3.5	8.4	19.4	18.9
	7	-	21.6	4.0	25.8	51.4	57.8	36.2	26.1	27.7	90.0	-	6.8	7.6	7.2	21.6	-
September 1975	5	12m	17.5	3.8	27.8	49.1	49.4	19.0	12.6	16.7	48.3	48.0	7.7	3.6	8.6	19.9	-
	8	sfc	19.8	8.4	25.8	54.0	49.7	22.5	20.6	13.7	56.8	55.5	9.5	-	7.0	-	23.3
	8	5m	28.4	<0.4	21.0	49.4	50.4	25.1	14.7	16.2	56.0	50.4	6.4	4.9	7.9	19.2	20.9
November 1975	9	sfc	29.9	2.5	32.4	64.8	68.7	38.1	22.0	12.6	72.7	74.4	8.0	7.5	8.8	24.3	28.4
	8	sfc	18.2	2.9	29.9	51.0	51.5	23.1	16.2	18.3	57.6	53.9	6.7	5.5	8.0	20.2	22.1
	9	6m	32.5	4.9	20.4	57.8	51.5	-	-	-	-	-	8.8	5.6	7.8	22.2	24.6
	8	9m	15.0	8.2	23.5	46.7	45.9	24.1	-	12.7	-	44.0	7.1	-	6.2	-	17.8
	Mean		21.2	3.5	28.4	53.1	53.6	25.2	18.4	16.8	60.8	55.1	7.4	4.7	8.2	20.7	21.8
	(std. dev.)		±4.8	±2.5	±4.1	±4.9	±6.2	±9.5	±7.7	±4.5	±15.7	±14.4	±0.9	±1.7	±0.9	±1.6	±3.0
	% of total		39.9	6.6	53.5	100	-	41.7	30.5	27.8	-	-	36.4	23.2	40.4	-	-

(Note: all samples had < 0.5 ppm Exch. Ni, Pb and Co)

Reducible, oxidizable and residual Fe concentrations in river-mouth particulates from varying salinities are statistically equal to those of the river suspended matter. The data show that "free" Fe oxide and lattice-held Fe concentrations are roughly equivalent and that together they constitute >93% of the total particulate Fe. Delta suspended matter with high organic matter content (e.g. September and November samples) had lower residual Fe concentrations due to dilution of the aluminosilicate matrix. However, because delta POC and metal analyses were not always done on the same sample it is difficult to quantify the dilution effect as was done with the river particulates.

No detectable alterations in Fe partitioning occur across the freshwater-seawater mixing zone from the river to the delta (Fig. 14a). This is, in one respect, reasonable because even if all the river dissolved Fe were to precipitate on only 1% of the river suspended matter, Gulf of Mexico particulate Fe concentrations would increase by only 0.1% (i.e. a 2% relative increase).

Lattice-held Mn concentrations in both the river and nearshore Gulf samples average 105 ppm. Similarly, the oxidizable Mn in both data sets is equivalent at about 30 ppm. Exchangeable Mn concentrations, however, are significantly higher in the delta suspended matter. This is best explained by the good correlation (0.81) of exchangeable Mn with organic carbon and the higher organic content of the delta samples (Fig. 14b). Further support for the association of exchangeable Mn with organic matter is derived from the high values measured for the organic-rich river samples (Table 7).

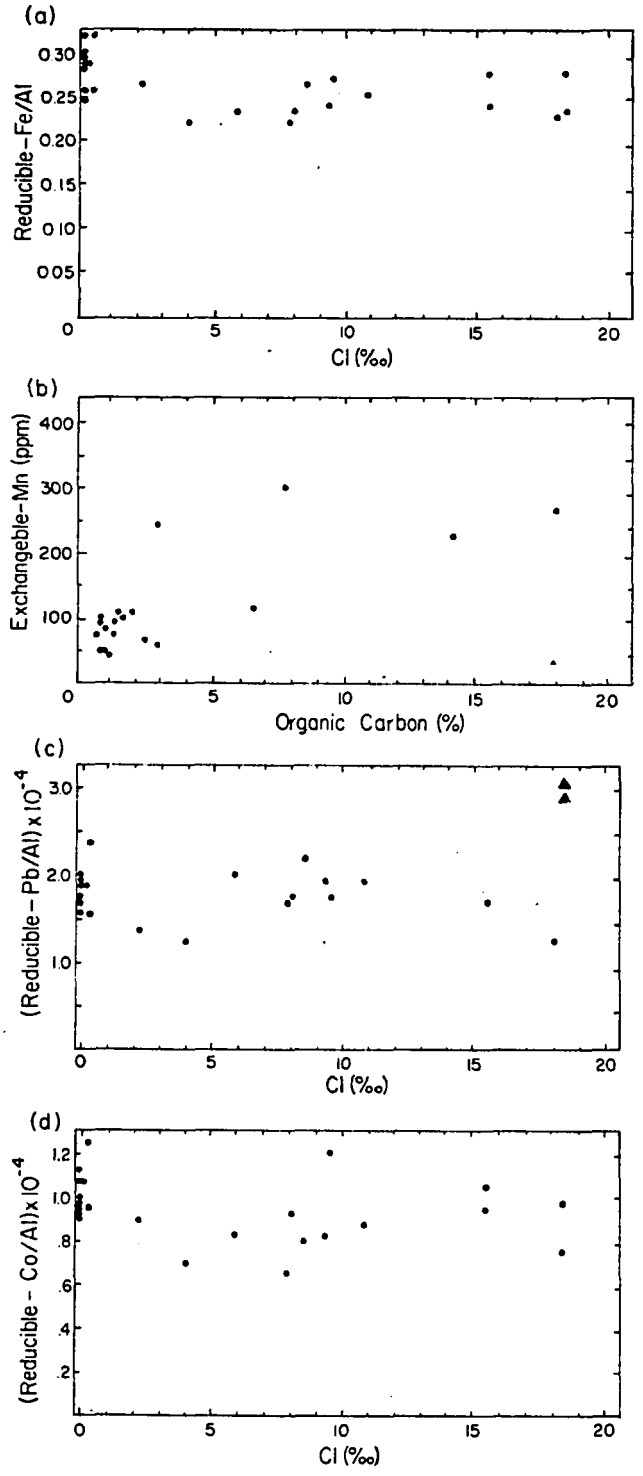


Fig. 14. a-d. Metal partitioning across the freshwater-seawater interface at the mouth of the Mississippi River. (a) Reducible-Fe/Al vs. chlorinity. (b) Exchangeable Mn vs. organic carbon. (c) Reducible-Pb/Al vs. chlorinity. (d) Reducible-Co/Al vs. chlorinity.

Reducible Mn concentrations in the delta suspended matter are variable (950 ± 243 ppm) and average 200 ppm lower than the river particulates. In some samples the decrease in reducible Mn is coupled with an increase in the exchangeable fraction. This suggests that some of the Mn-oxide material is removed to exchangeable surface positions during transport to the marine environment.

Delta suspended matter total Cu concentrations are 23% higher than those for the river particulates, yet lattice-held concentrations are equivalent at 14.4 and 14.0 ppm respectively. Oxidizable Cu concentrations for the river (12.7 ppm) and delta (13.2 ppm) particulates are also alike. An increase in the reducible fraction thus accounts for the observed higher Cu values in the delta suspended matter. This increase in reducible Cu concentrations conflicts with previously suggested Cu-organic matter relationships. One possible explanation for this disparity is that organic complexes are susceptible to attack by citrate-dithionite. Exchangeable Cu concentrations behave analogously to those for Mn and the two are significantly correlated ($r = 0.72$). Three delta samples had high total Cu concentrations with increased percentages of reducible and oxidizable Cu, yet comparable residual concentrations. Thus, the 25% higher Cu levels in the delta particulates may be due to Cu adsorption/coprecipitation on oxides and organic Cu chelation.

Nickel partitioning in delta particulates parallels that of the river samples in both absolute concentrations and percentages of total Ni. Oxide phase and lattice Ni account for 94% of the total Ni present. No evidence of alteration of particulate Ni concentrations across the freshwater-seawater boundary was found.

Five samples in the Pb data set (Table 17) are possibly contaminated since they had very high Pb concentrations. These were analyzed to determine the effect of contamination on metal partitioning. Three of these samples had lattice-held Pb concentrations of 15 ppm, in good agreement with concentrations for delta (15.7 ppm) and river particulates (14.8 ppm). Two had high residual levels (26 ppm). By discarding these five samples from the delta population, Pb partitioning is statistically equivalent to that found in the river particulates:

	Pb (ppm)		
	Red.	Ox.	Res.
River particulates	20.3	14.4	14.8
Delta particulates (excluding 5 samples)	20.9	15.2	15.7

Thus, no uniform, predictable change in particulate Pb concentrations is observed across the freshwater-seawater interface from the river to the delta (Fig. 14c).

Delta particulate Co concentrations were 8.2 ppm in the residual phase and 4.7 ppm in the oxidizable fraction. These concentrations are similar to those for river particulates (8.1 and 4.6 ppm respectively). Reducible Co in the delta particulates was 19% lower than that from the river. This amounts to only a 1.4 ppm difference and thus the two data sets are not statistically different (Fig. 14d).

Mississippi Delta Sediments: Metal Distribution

Heavy metal concentrations for 88 Mississippi Delta and upper fan sediments are summarized in Table 18. The complete data set is

Table 18. Mississippi Delta and upper fan sediment metal, $CaCO_3$ and grain size distribution

Station	N	Water depth (m)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	$CaCO_3$ (%)	Silt (%)	Clay (%)	S $g\,cm^{-2}\,y^{-1}$
17	6	20	3.04 (±0.51)	6.56 (±0.55)	725 (±170)	101 (±18)	27.2 (±3.9)	24.2 (±4.9)	12.7 (±2.4)	80 (±13)	39.8 (±6.1)	-	-	0.8 (±0.3)	47.7 (±3.2)	21.6 (±5.0)	-
8	13	30	3.99 (±0.27)	7.83 (±0.27)	657 (±55)	132 (±11)	38.6 (±3.2)	30.6 (±1.7)	15.8 (±1.4)	78 (±7)	40.5 (±3.3)	1.0 (±0.2)	124 (±9)	0.2 (-)	39.9 (±3.3)	58.2 (±5.8)	>2
10	11	50	4.13 (±0.17)	8.01 (±0.30)	769 (±69)	139 (±10)	42.5 (±5.3)	32.3 (±2.7)	16.8 (±1.8)	83 (±14)	41.8 (±2.4)	1.3 (±0.2)	-	0.5 (-)	38.9 (±4.0)	60.9 (±4.1)	>2
12	9	60	3.99 (±0.22)	8.07 (±0.38)	655 (±51)	135 (±10)	37.5 (±4.7)	30.3 (±2.9)	14.6 (±1.4)	91 (±16)	45.5 (±2.5)	-	130 (±10)	0.6 (±0.2)	45.8 (±2.6)	52.2 (±3.4)	1.3
16	12	110	4.24 (±0.24)	8.35 (±0.19)	724 (±389)	127 (±9)	35.6 (±6.2)	26.0 (±1.0)	16.3 (±1.7)	79 (±9)	38.6 (±3.5)	0.5 (±0.2)	145 (±24)	1.0 (±0.2)	28.8 (±1.4)	71.0 (±1.3)	0.5
11B	7	130	4.03 (±0.20)	8.21 (±0.22)	631 (±74)	132 (±7)	36.6 (±5.9)	28.1 (±1.7)	14.7 (±0.6)	94 (±9)	47.0 (±5.3)	-	153 (±13)	0.3 (-)	40.4 (±3.5)	59.2 (±3.7)	1.1
14	11	150	3.94 (±0.10)	8.35 (±0.14)	1400* (±390)	120 (±3)	28.7 (±3.4)	23.0 (±0.7)	15.0 (±1.5)	-	35.6 (±3.9)	-	154 (±9)	1.9 (±0.2)	29.4 (±1.6)	70.4 (±1.7)	0.35
11A	8	480	4.02 (±0.16)	8.61 (±0.29)	726* (-)	119 (±7)	27.0 (±7.0)	26.9 (±1.7)	14.1 (±1.6)	88 (±5)	39.7 (±2.7)	-	150 (±13)	2.5 (±0.8)	34.2 (±5.1)	65.4 (±5.3)	0.15
15	11	550	4.04 (±0.36)	8.48 (±0.42)	1670* (±210)	118 (±9)	26.0 (±6.3)	26.3 (±2.6)	14.8 (±1.2)	-	40.4 (±4.7)	0.3 (±0.1)	-	1.9 (±0.4)	26.5 (±4.1)	73.4 (±4.0)	0.06
Mean, N=88 (Std. dev.)			3.99 (±0.37)	8.11 (±0.58)	743† (-)	125 (±13)	33.7 (±7.7)	27.7 (±3.6)	15.0 (±1.8)	84 (±12)	40.6 (±4.9)	0.8 (±0.5)	141 (±17)	1.1 (±0.8)	36.6 (±7.7)	60.2 (±14.2)	≈1 (-)
Range			4.46 to 2.34	8.90 to 5.84	7950* to 343	155 to 74	55.5 to 18.8	34.7 to 18.0	19.5 to 10.0	108 to 63	54.9 to 29.2	1.6 to 0.05	167 to 110	3.4 to 0.2	50.4 to 22.6	77.2 to 15.8	>2 to 0.06

* Data set includes surface and/or subsurface Mn enrichment.

† Mean does not include Mn-rich sediment values.

given in APPENDIX E and station locations are shown in Fig. 15. Metal concentrations are relatively uniform throughout most of this nearshore area with the exception of Mn and Cd. Observed minimum values are restricted to the few sand-rich layers (~25% sand) sampled immediately outside the Mississippi River mouth (Station 17) and thus the mean values presented in Table 18 are quite representative of the delta sediments as a whole.

Several general trends were observed for the nearshore sediment data (Table 18 and APPENDIX E). $CaCO_3$ percentages increase gradually (from 0.2 to 3.4% total $CaCO_3$) seaward of the Mississippi River as the massive terrigeneous input of the river decreases relative to surface water productivity. A similar, but less obvious trend for organic carbon shows that higher values (from the overall range of 0.3-1.0% organic C) are more frequent in offshore areas (TREFRY, 1974; ARMSTRONG, 1974). The percentage of clay-size particles (<2 μm) increases from <50 to 70% seaward of the river as a function of physical transport processes. There are no distinct areal variations in average sediment Fe, Co, Cr or Ni values (Table 18); however a slight increase in Al and V concentrations and a slight decrease in Cu concentrations is found seaward of the river. Average Pb and Cd concentrations are higher in shallow-water cores due to the greater sediment depth at which pollutant levels are found (TREFRY and PRESLEY, 1976a). Higher Zn values found in shallow areas may also reflect anthropogenic input. Surface Mn enrichment is observed in sediments from the outer perimeter of the delta platform and is related to diagenetic Mn remobilization.

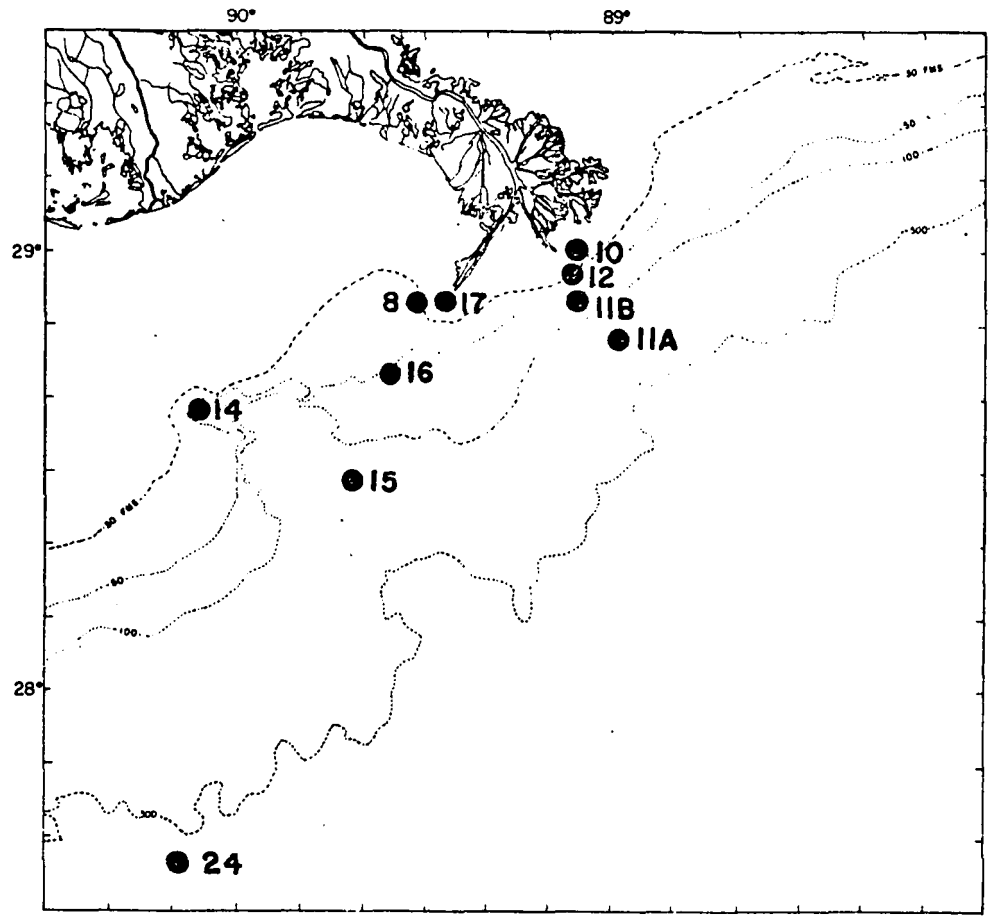


Fig. 15. Mississippi Delta, upper fan and slope sediment sampling sites.

Delta sediment metal concentrations from this study are surprisingly close to those determined by previous investigators (Table 19). One exception to this is Ni. Mississippi silt metal concentrations reported in the classic work of CLARKE and STEIGER (1914) and given in Table 19 are lower than normally reported for delta sediments. These lower values are similar to those reported by this study for Mississippi Delta shallow-bay sediments and are due to the less clay-rich (∿35% clay) nature of the material analyzed. Table 19 also shows that delta sediments have lower Fe, Cu and Ni concentrations than average continental crust or shale yet higher Zn, Pb and Cd values. Delta sediment Al, Co, Cr, V and Ti content is equivalent to crustal data. These trends agree with those discussed for river particulates. Sediment Mn concentrations (743 ppm), however, are lower than average shale, a significant reversal from the 1300 ppm suspended matter values.

Vertical profiles of metal concentrations in sediments from the Mississippi River mouth, the delta platform and the upper fan depict some of the above trends and provide an initial overview of metal distribution in these three nearshore environments. Metal concentrations are normalized to Al to correct for sediment changes in $CaCO_3$, salt content and mineralogy. Normalization to Fe can be used with equal effectiveness in these sediments as outlined by TREFRY and PRESLEY (1976a). Geochronologies are also given for each core using predominantly the Pb-210 data of SHOKES (1976).

Station 17 sediment depicts the heterogeneous nature of the near

Table 19. Reported metal concentrations for Mississippi River Delta sediments

	No. of samples	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	V (ppm)	Ti (%)
Miss. Silt (CLARKE and STEIGER, 1914)	235	2.43	5.57	460	-	-	34	-	68	130	140	0.32
Miss. Delta-Fan (YOUNG, 1954)	19	-	-	-	-	-	-	16	84	49	137	0.36
W. Miss. Delta (POTTER et al., 1963)	8	-	-	-	-	24	27	-	70	40	138	-
Miss. Delta, outer shelf NW Gulf (DAVIS, 1968)	8	-	-	705	109	49	27	-	-	86	-	-
Miss. Cone (TIEH and PYLE, 1972)	15	3.69	-	1045	57	-	-	-	-	96	-	0.48
W. Miss. Delta bore holes (TIEH et al., 1973)	6	4.26	-	700	-	-	-	-	-	55	-	0.39
Miss. shallow bays (this study)	13	3.10	6.63	630	-	26	24	18	62	29	100	-
Miss. Delta (this study)	88	3.99	8.10	743	125	34	28	15	84	41	141	0.42
Continental crust (TAYLOR, 1964)	-	5.63	8.23	950	70	12.5	55	25	100	75	135	0.57
Average shale (TUREKIAN and WEDEPOHL, 1961)	-	4.72	8.00	850	95	20	45	19	90	68	130	0.46

river mouth deposits which are accumulating at ∿10 g cm^{-2} y^{-1} (COLEMAN, personal communication). Metal concentrations in sediment from Station 17 (Fig. 16) are generally low. These low values are associated with a significant river-bedload derived sand component. The vertical profiles in Fig. 16 also point out the significant covariance among metals. This is especially evident in the surface sand layer and the higher clay-bearing 20-25 cm section.

Fig. 17 illustrates vertical metal distribution in the more uniform, yet rapidly accumulating (1-2 g cm^{-2} y^{-1}; SHOKES, 1976) sediment of the mid-delta area. The Fe/Al ratio is very constant throughout the sediment column implying uniform mineralogical composition. No Mn-rich layers are found at Station 12, however, there is observable covariance of Mn with Ni and Co. Zinc and Cu, on the other hand, appear to follow Fe more closely than Mn. Lead concentrations are distorted by polluted levels throughout most of the core.

Station 14 sediment from the outer Mississippi Delta has a 15 cm surface oxidized zone with high (2260 ppm), diagenetically-induced Mn concentrations (Fig. 18). A corresponding 6 cm Mn-rich (1860 ppm) zone is also found in surface sediment from outer delta Station 16. However, even the top millimeters of sediment from another outer delta site (11B) have low Mn concentrations (576 ppm). Each of the three sites (Fig. 15, Table 18) are from similar water depths yet have different sediment accumulation rates (Sta. 14, 150 m, 0.35 g cm^{-2} y^{-1}; Sta. 16, 110 m, 0.5g cm^{-2} y^{-1}; Sta. 11B, 130 m, 1.1 g cm^{-2} y^{-1}). Thus, it appears that the formation of a measurable Mn-rich oxidized zone in the delta sediments commences when sedimentation

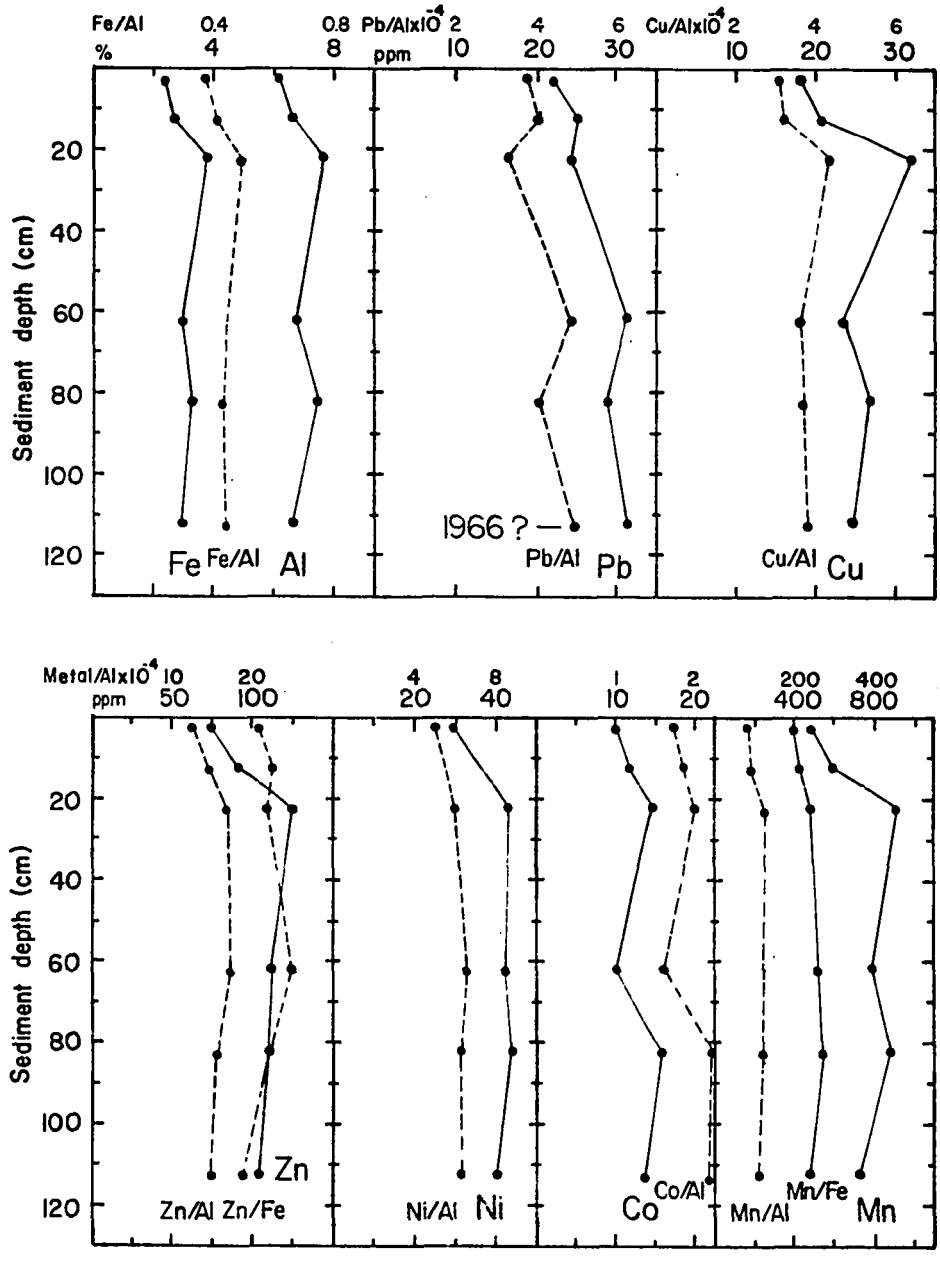


Fig. 16. Vertical metal profiles for Station 17 sediment (water depth 20 m).

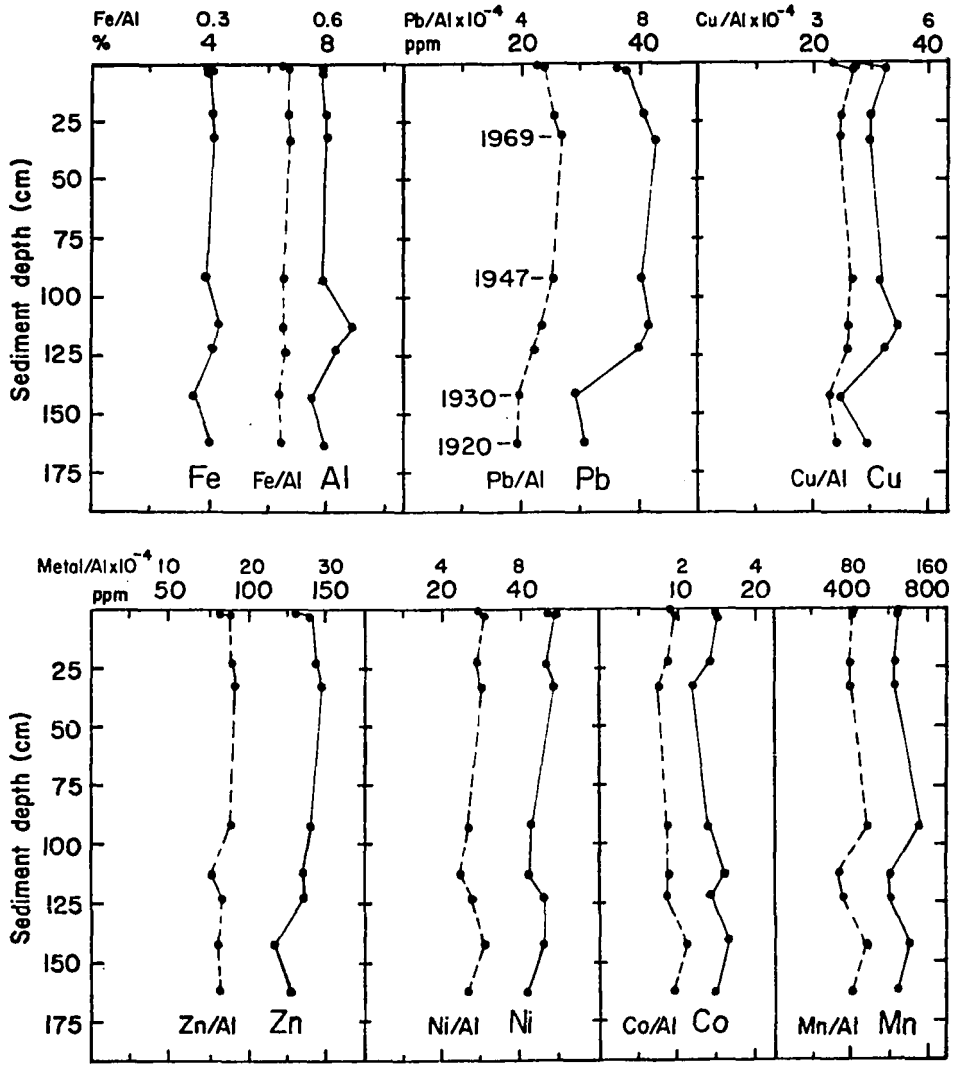


Fig. 17. Vertical metal profiles for Station 12 sediment (water depth 60m). Dates based on Pb-210 geochronologies (SHOKES, 1976).

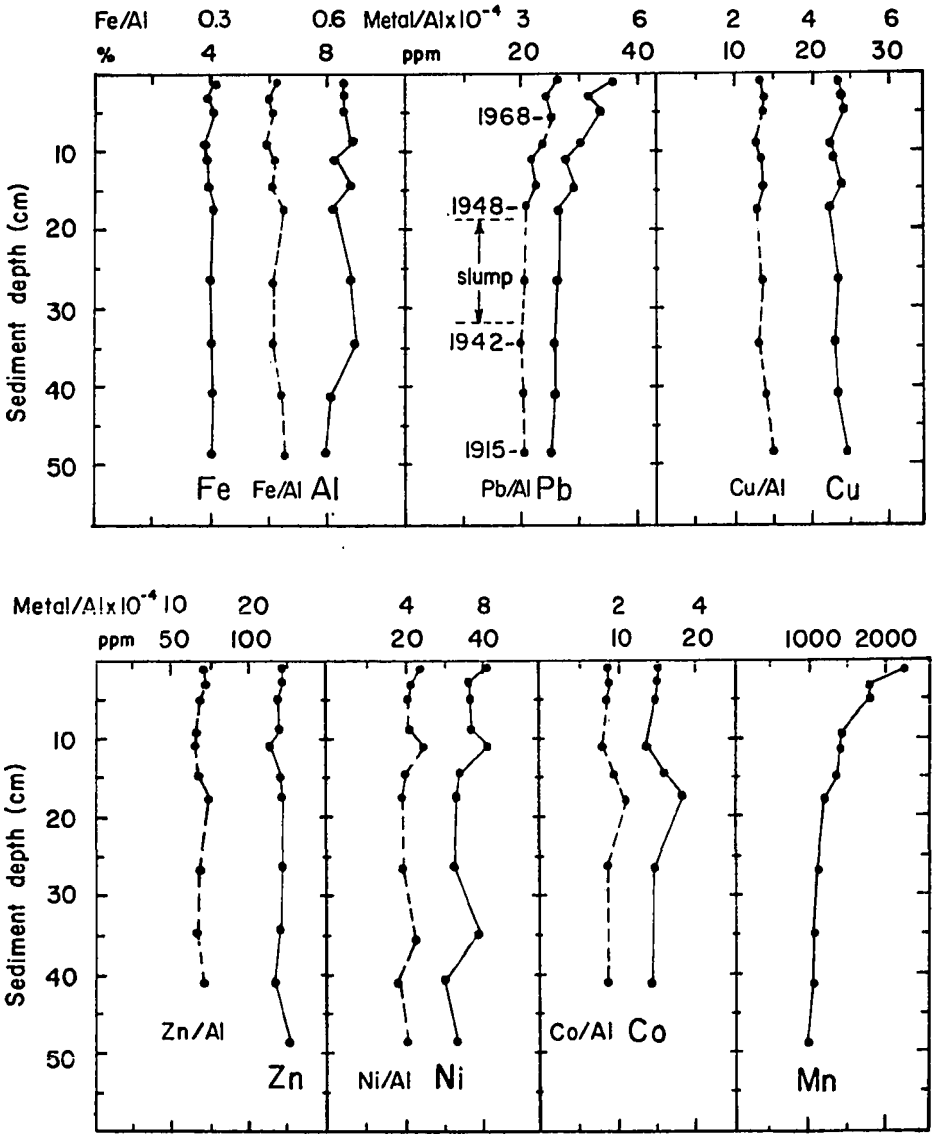


Fig. 18. Vertical metal profiles for Station 14 sediment (water depth 150 m).

rates of less than 0.5-1.0 g cm^{-2} y^{-1} are encountered. Conversely, where sediments accumulate faster than 0.5-1.0 g cm^{-2} y^{-1} no surface Mn-rich layer forms. Fig. 18 also shows a characteristic Pb-rich zone which will later be shown to have a time-dependent distribution suggesting pollutant input. Concentrations of the other metals at Station 14 are uniform throughout the core. This vertical homogeneity is typical of outer delta sediments.

Upper Mississippi Fan sediment (Stations 11A and 15) accumulates at about 0.1 g cm^{-2} y^{-1} and is characterized by a surface Mn-rich zone (Fig. 19). Station 15 surface Mn values, for example, are 7950 ppm. Lead levels are above normal only in the top 25 cm of these fan sediments. Each of the other metals appears to have a recent history of constant deposition of very similar concentration material.

Interelement covariance in nearshore sediments is examined more thoroughly in the correlation coefficients matrix given in Table 20 and the subsequent scatter plots (Fig. 20). Fig. 20a shows expected significant positive correlations (at $p<0.01$) of Fe and Al concentrations with clay (<2 μm particles) percentages. However, Fig. 20a also shows a difference in slope for the two metals versus clay. The slope differences indicate a more rapid increment in percent Fe content in the clay minerals (relative to Al) and/or an increased Fe oxide coating on clays. Thus, the extrapolated Fe/Al ratio for clay-free sediment of 0.40 increases to 0.51 in delta sediment with two-thirds clay.

Significant correlations of Fe with Al, H_2O content, Zn (Fig. 20b)

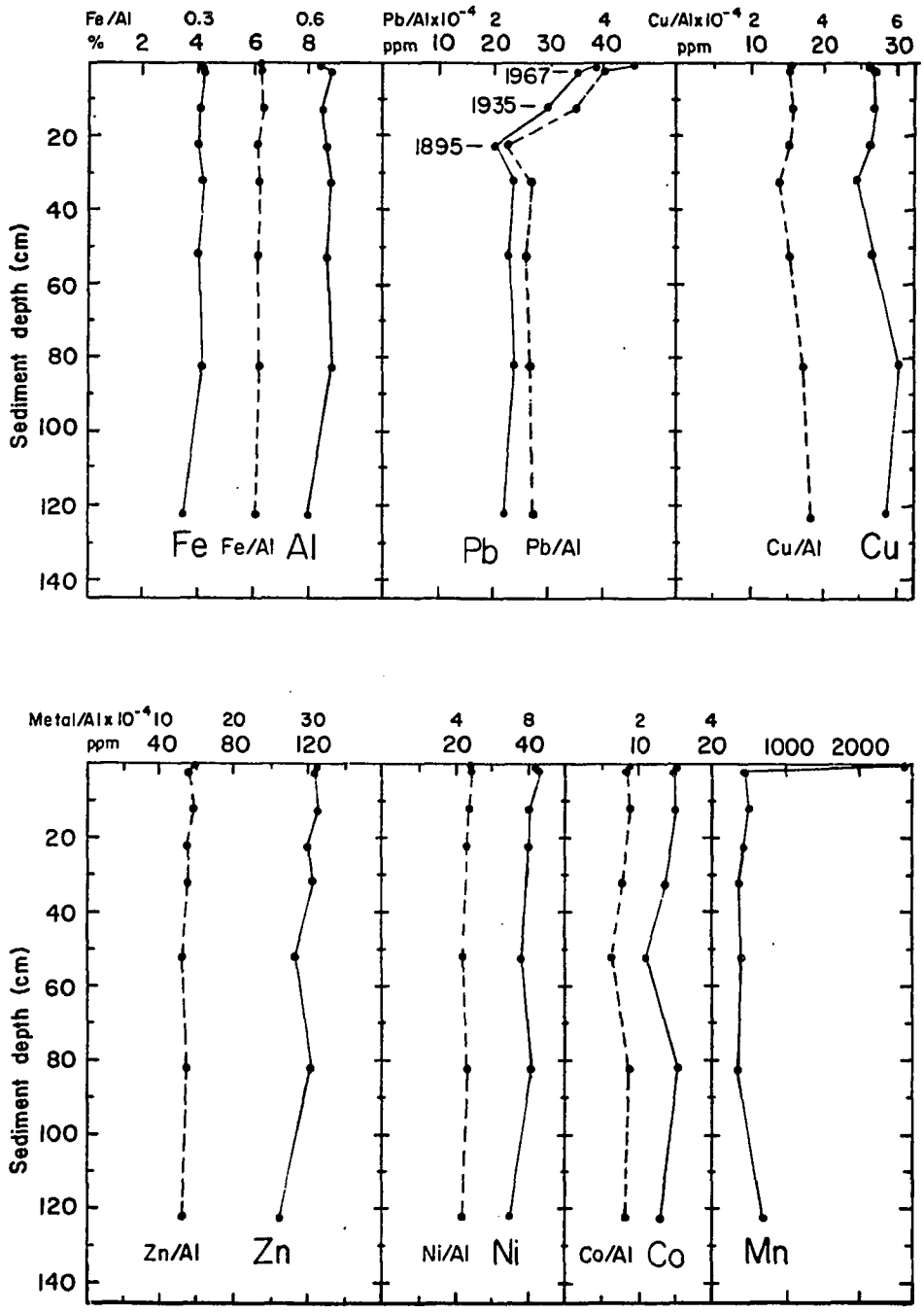


Fig. 19. Vertical metal profiles for Station 11A (water depth 480 m). Dates based on Pb-210 geochronologies (SHOKES, 1976).

Table 20. Correlation coefficients matrix for Mississippi Delta sediment data*

	Z	Fe	Al	Mn	Zn	Pb	Cu	Co	Cr	Ni	Cd	V	$CaCO_3$	H_2O	Sand	Silt	Clay
Z†	1.00																
Fe	-0.30	1.00															
Al	-	0.83	1.00														
Mn	-	-	-	1.00													
Zn	-	0.73	0.48	-	1.00												
Pb	-	0.42	-	-	0.73	1.00											
Cu	-	0.43	-	-	0.72	0.63	1.00										
Co	-	0.40	-	-	0.39	-	-	1.00									
Cr	-	-	-	-	-	-	-	-	1.00								
Ni	-	0.33	-	-	0.53	0.51	0.45	-	0.53	1.00							
Cd	-	-	-0.48	-	0.78	0.83	0.91	-	-	0.50	1.00						
V	-	-	-	-	-	-	-	-	-	-	-	1.00					
$CaCO_3$	-	-	0.41	0.38	-0.32	-0.50	-0.55	-	-	-	-0.80	0.81	1.00				
H_2O	-0.41	0.60	0.68	0.29	0.41	-	-	-	-	-	-	-	0.41	1.00			
Sand	-	-0.89	-0.92	-	-0.68	-	-0.48	-0.57	-	-	-	-	-	-0.72	1.00		
Silt	-	-0.49	0.62	-	-	-	-	-	-	-	-	-	-0.51	-0.63	0.48	1.00	
Clay	-	0.82	0.91	-	0.47	-	-	0.55	-	-	-	-	-	0.79	-0.88	-0.84	1.00

* Only correlations significant at $p < 0.01$ are listed.

† Z = sediment depth.

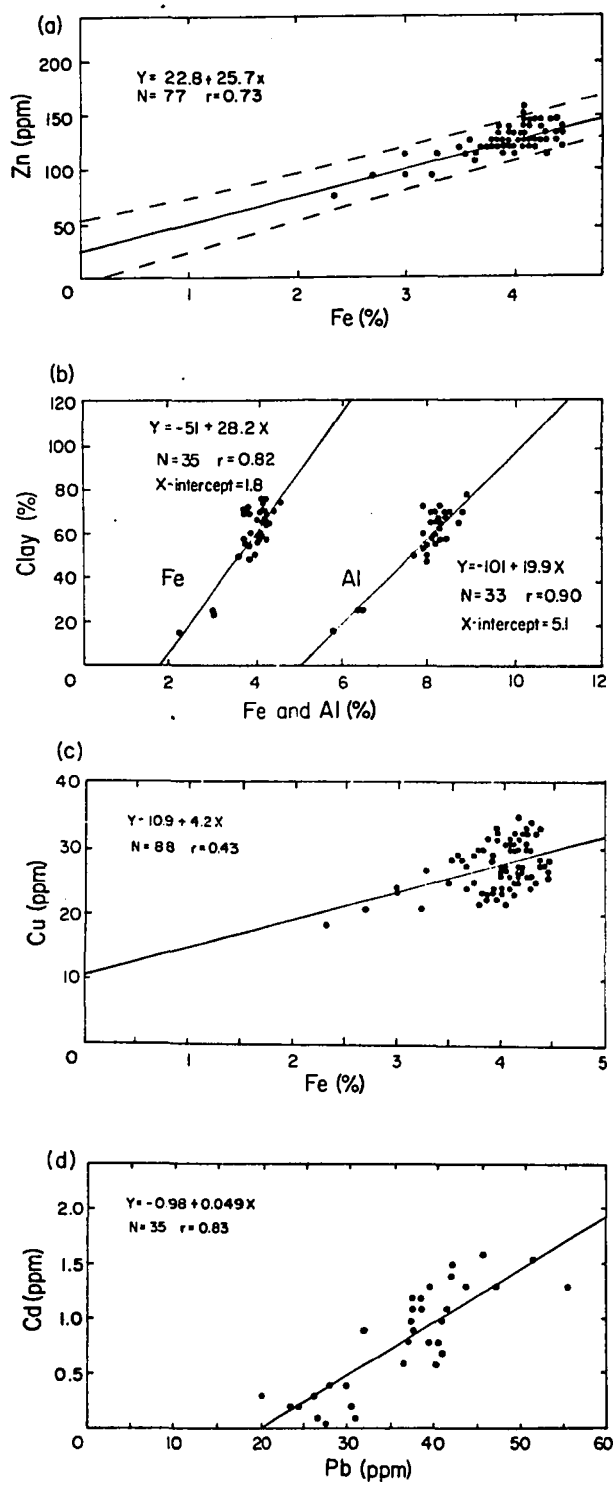


Fig. 20. a-d. Selected scatter plots for Mississippi Delta sediment metal data. (a) Zn vs. Fe. (b) Clay vs. Al. (c) Cu vs. Fe. (d) Cd vs. Pb.

and to a lesser degree with some of the other metals (Fig. 20c) were also found. For some of the trace metals, the narrow range of measured values (for example, Cu, Fig. 20c) often allows small variations in concentrations to lower correlation coefficients. Narrow ranges are distorted by the analytical precision, slight changes in mineralogical composition and possible differential post-depositional mobility of elements. Other inter-element correlations (e.g. Cd/Zn, Cd/Cu, Pb/Zn, Table 20; Cd/Pb, Fig. 20d) show that covariance among the trace metals may be related to some of the more subtle mineralogical variability as well as anthropogenic inputs.

Factor analysis was also applied to the nearshore sediment data because it reduces the numerous relationships found among many variable to simpler relationships among fewer variables. The factor program used (BARR et al., 1976), like others, takes the initial correlation matrix, diagonalizes it, and solves for eigenvalues, and for vectors which are linear combinations of the original variables. Each vector (or factor) successively maximizes the explained variance for each variable. The end result is a grouping of variables that are highly correlated. Sediment metal distribution which is explained by a single factor (e.g. Fe and Al, Table 21) is probably controlled by a single process. Metals with more complicated factor patterns (e.g. Mn and Ni, Table 21) may have a more complex distribution.

For the Mississippi Delta sediments studied, four factors explain 87% of the sample variance (Table 21). Factor 1, with high

Table 21. Factor analysis for Mississippi Delta sediment data*

	Factor 1	Factor 2	Factor 3	Factor 4
Fe	0.96			
Al	0.92			
Mn		-0.50	0.61	0.45
Zn	0.77	0.55		
Pb	0.39	0.75		
Cu	0.51	0.68		
Co	0.69			0.49
Ni	0.35	0.56	0.51	-0.41
$CaCO_3$		-0.78	0.43	
Sand	-0.93			
Silt	-0.56	0.70		
Clay	0.88	-0.40		
Eigenvalues	6.130	3.296	1.122	0.788
Relative % of total	47.2	25.4	8.6	6.1
Cumulative %	47.2	72.5	81.1	87.2

* Loadings <0.3 omitted.

loadings for Fe, Al and clay, clearly describes the clay-rich, aluminosilicate detritus of the Mississippi River with associated metals (Zn, Co and Cu). Factor 2, with negative loadings for Mn, $CaCO_3$, and clay, characterizes very near-river-mouth sediments where there is pollution (Pb and perhaps Zn) and a greater predominance of heavy minerals (in the silt fraction) with associated metals (Ni, Zn and Cu). Factor 3 is associated with the Mn-rich zones found in the higher carbonate content outer-shelf and fan sediments and shows the liklihood of Ni remobilization along with Mn. Factor 4 is not easily explained. In summary, ~50% of the variance in these nearshore sediment metal concentrations is explained by an association of metals with aluminosilicates. The remainder of the variance is described by pollution, physical sorting of particles and post-depositional remobilization of metals.

Delta sediment Mn, Zn, Pb, Cu, Co, Ni and Cd concentrations are 20-50% lower than river particulate values (Table 22) whereas Fe, Al, Cr and V concentrations are within 10% of river particulate values. Sediment Pb and Cd averages are lower because pollutant levels diminish with sediment depth (or time) and therefore only surface Pb and Cd values are comparable with river particulate concentrations. Surface sediment averages for each of the other elements are more consistent with the overall sample means. Thus, Mn, Zn, Cu, Co and Ni still appear depleted in the nearshore sediments relative to river particulates.

Suspended matter and nearshore sediment metal values may be compared by normalizing metal values to Al and calculating the change

Table 22. Comparison of total metal concentrations in Mississippi River particulates with Mississippi Delta sediments

		Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Clay (%)	$CaCO_3$ (%)	Organic Carbon (%)
River suspended matter (RSM)	Mean (N=43)	4.61	8.65	1300	193	46	45	21	79	55	1.3	152	59.0	0.5	2.0
	(metal/Al) x 10^4	5,330	-	150	22.3	5.3	5.2	2.4	9.1	6.4	0.15	17.6	-	-	-
Delta sediments (DS)	Mean (N=88)*	4.22	8.59	758†	133	36	29	16	88	43	0.8	149	60.2	1.2	0.9
	(metal/Al) x 10^4	4,910	-	88	15.5	4.2	3.4	1.9	10.2	5.0	0.09	17.4	-	-	
Delta surface sediments	Mean (N=8)*	4.51	8.88	661†	141	44	29	16	94	49	1.1	149	64.7	1.2	-
	(metal/Al) x 10^4	5,080	-	74	15.9	5.0	3.3	1.8	10.6	5.5	-	16.8	-	-	-
	δM (%)[‡]	-8	0	-41	-29	-6	-35	-21	+12	-22	-	-1	-	-	-

* Metal values calculated salt-free, $CaCO_3$-free.

† Not including Mn-rich zones.

‡ $$\delta M = \left[\frac{\text{metal}/(\text{Al})_{DS}}{\text{metal}/(\text{Al})_{RSM}} - 1\right] \times 100$$

(δM) in metal concentration which occurs between the two environments. Aluminum concentrations are virtually unchanged across the deposition zone. Low δM values for V and Pb suggest that these species are rather immobile. A positive value for Cr may result from physical sorting of minerals or an unrepresentative data set. Large negative δM values for Mn, Zn, Cu, Co and Ni suggest either that fine-grained sediment coated with these metals has bypassed the delta or that chemical reduction-diffusion has removed a significant fraction of these metals from the nearshore environment. A negative δM for Fe, although small, implies a large change in concentrations on a ppm scale. The apparent loss of some metals from delta sediments is significant and thus sediment leaching studies and interstitial water discussions will focus on this phenomenon.

Mississippi Delta Metal Pollution

Mississippi River and Delta pollution has been previously referenced, implied or held responsible for observed metal trends. Estimates of industrial, municipal and agricultural waste inputs to the Mississippi River (EVERETT, 1971) suggest that the river pollutant load is large and diverse. Such input could affect the heavy metal geochemistry of the river and the delta. Thus, pollution findings from other studies and the history of metal input to the delta as determined from this study will be considered below.

Organic contaminants have most often been cited as troublesome in the Mississippi River. Fish kills during the 1950's were attributed to the insecticides endrin and heptachlor (LA. WILDLIFE and FISH. COMM., 1958-1959). Recent data show that river phenol concentrations consistently exceed public water supply criteria (U.S. ARMY CORPS OF ENGINEERS, 1975)

and that the river has a significant anthropogenic input of light hydrocarbons (BROOKS, 1976) and phthalic acid esters, DDTs and PCBs (GIAM et al., 1976). Added to this load is the domestic sewage from almost 2 million people in the lower Mississippi area alone. Because many of the organics use oxygen as they degrade in the river, a progressive decrease in dissolved oxygen concentrations has been measured downstream from Baton Rouge to the Gulf (EVERETT, 1971).

In addition to organic substances, an estimated 18 million kilograms of inorganic wastes are discharged into the lower Mississippi River daily (EVERETT, 1971). This flux is equivalent to 7% of the total dissolved load at average river flow and 21% of the total at low flow. Little data is available on the composition of this industrial discharge; however such wastes are known to contain various heavy metals (NATL. ACAD. SCI., 1975). TREFRY and PRESLEY (1976a, 1976b) found evidence of Pb and Cd pollution in sediments from an extensive area of the Mississippi Delta. Results from the present study confirm these observations and provide a more reliable time scale for reexamining the history of delta metal pollution.

Mississippi River dissolved metal concentrations are low and except for Zn are considerably below those for established water quality criteria (Table 23). River particulate Zn concentrations are also higher than those accepted as suitable for dredged sediment disposal (Table 23). Although the dumping criteria are geochemically oversimplified and do not predict the biological availability of excess metal loads, they do point out pollutant metal levels. Zinc, Pb and Cd concentrations are also much higher in river suspended matter than in average continental crust (Table 23).

Table 23. Mississippi River dissolved and particulate metal concentrations and E.P.A. environmental quality criteria

Dissolved metal concentrations in µg/ℓ

	Fe	Mn	Zn	Pb	Cu	Ni	Cr	Cd	Hg
Mississippi River	10	10	10	<1	2	2	0.5	0.1	<0.1
Water Quality Criteria (EPA, 1973)	300	50	1	30	60	100	50	4	2
Ave. river water (TUREKIAN, 1974)	-	7	20	3	7	0.3	1	-	0.07

Particulate metal concentrations in µg/g

	Zn	Pb	Cu	Cd
Mississippi River	193	46	45	1.3
Sediment disposal Criteria (EPA, 1973)	75	50	50	2
Ave. crustal abundance (TAYLOR, 1964)	70	13	55	0.2

To establish a baseline for tracing the history of metal input to the Mississippi Delta, the Pb-210 geochronologies of SHOKES (1976) are superimposed on vertical sediment metal profiles from this study. Assigned dates are subject to the several assumptions of the Pb-210 method and the variability of the Mississippi Delta environment. One cannot resolve year-by-year dates but can isolate general time periods.

Fig. 21 for mid-delta Station 16 (see map, Fig. 15, p. 93) shows that Fe, Al, Cu, Zn, Ni and Co concentrations in these sediments have been uniform over the past 75 years. Lead concentrations, however, have increased by 65% during this time interval. The major onset of pollutant Pb has occurred since the mid-1940's, a period of increased usage of leaded gasoline. Surface sediment Pb concentrations ($\sim$45 ppm, salt-free, $CaCO_3$-free) at Station 16 are comparable with those of present-day river particulates (46 ppm). Observed flattening of the upper portion of the Pb curve (Fig. 21) might logically be ascribed to vertical mixing of sediment. However, comparable river particulate and Station 16 surficial sediment Pb values, constant Pb concentrations over 50 cm (and 10-15 y) in near river mouth sediments, and no obvious mixing in the Pb-210 profile for Station 16 do not support mixing in this instance. In addition to Pb, surface sediment Cd concentrations at Station 16 are also high at double their pre-1950 values. Moreover, the 0.4 ppm Cd baseline concentration is still in excess of values found in deeper (older) sediments on the delta. Mid-delta Stations 14 (Fig. 18, p. 99) and 11B support observations made at Station 16. The

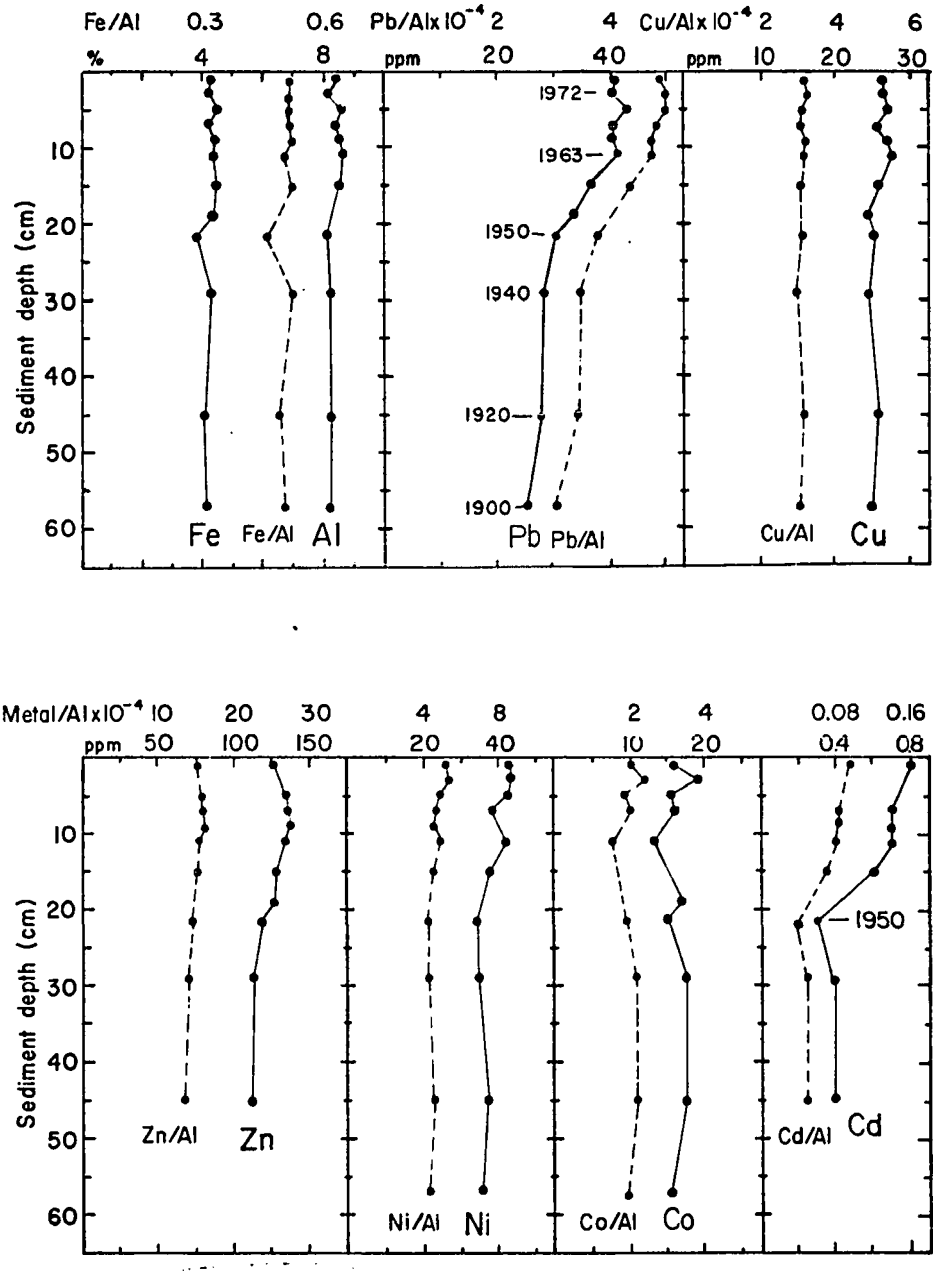


Fig. 21 Vertical metal profiles for Station 16 sediment, (water depth 110 m). Dates based on Pb-210 geochronologies (SHOKES, 1976).

stable Pb profile for Station 14 (Fig. 18), however, shows lower than expected surface Pb concentrations (and Pb/Al values). This surface decrease, when combined with the Pb-210 profile (SHOKES, 1976), supports vertical sediment mixing over the top 13 cm at this location.

Rapidly accumulating sediments (>3g cm^{-2} y^{-1}) from the near river mouth area of the delta have relatively straight vertical metal profiles (Fig. 22). Lead and Cd concentrations, however, are 70 and 200% respectively above base values found at Station 16 and are in good agreement with river particulate concentrations. Sediment Pb and Cd concentrations of >40 ppm and >1 ppm respectively for 50-60 cm profiles in this area indicate that the pollutant levels have been relatively constant during the past 10-15 years.

Outer delta sediments from Station 15 (Fig. 23) and Station 11A (Fig. 19, p.101), where accumulation rates are on the order of 0.1 g cm^{-2} y^{-1}, also have relatively constant Fe, Al, Cu, Zn, Ni and Co concentrations, or at least uniform metal/Al ratios. High surface Mn concentrations follow a geochemical, rather than a time-dependent distribution and are due to post-depositional reduction of Mn, upward diffusion and surface reoxidation. Lead concentrations at Station 15 (Fig. 23) decrease from 43 ppm (salt-free, $CaCO_3$-free) at the surface to 20-25 ppm in the lower core section. The time scale for this sample, however, permits an extension of the historical record and shows that the initial onset of pollutant Pb occurred during the mid-1800's. This

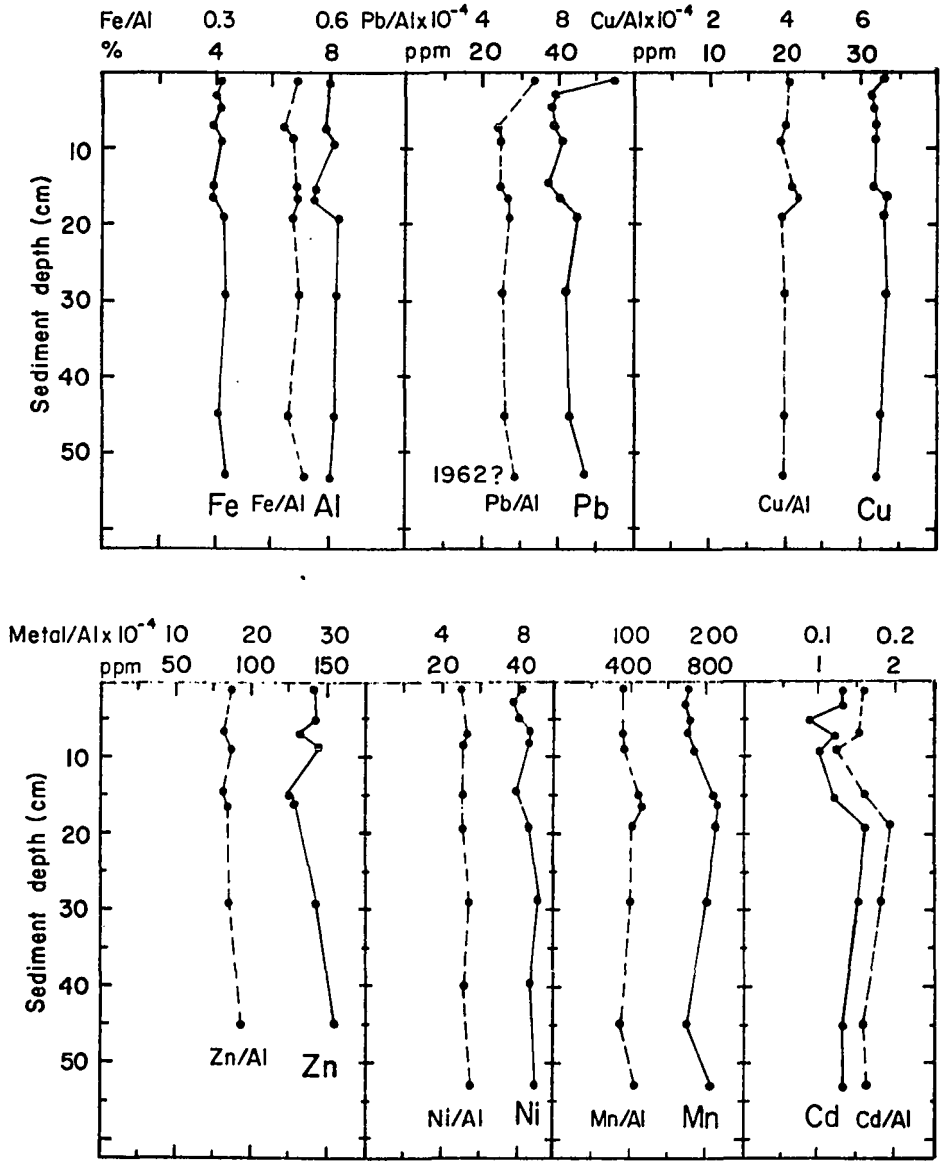


Fig. 22. Vertical metal profiles for Station 10 sediment (water depth 50 m).

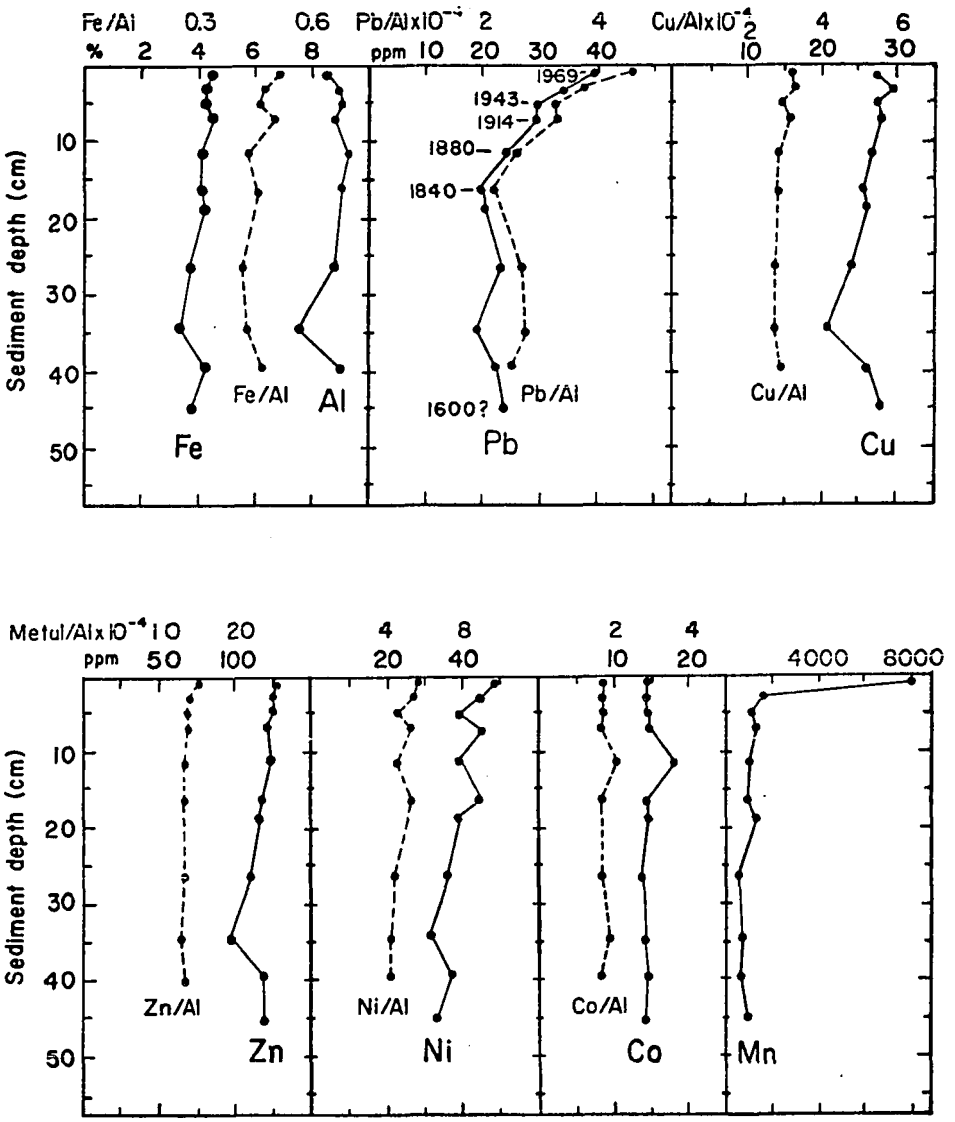


Fig. 23. Vertical metal profiles for Station 15 sediment (water depth 550 m). Dates based on Pb-210 geochronologies (SHOKES, 1976).

initial flux is followed by the previously observed period of increase during the mid-1940's. The Station 11A Pb profile (Fig. 19) is similar and both are consistent with Pb profiles for Lake Michigan sediments presented by EDGINGTON and ROBBINS (1976) who attribute excess Pb deposited prior to 1920 to inputs from the combustion of coal.

Chemical Partitioning of Metals in Delta Sediments

Chemical partitioning data for 15 of the 88 Mississippi Delta sediments (Table 24) provide a sample subset with total metal concentrations which cover the range of observed values. Mean values, however, are skewed to the low side. For example, total Fe values in the 15 leached samples ($\bar{x}$ = 3.68% Fe) are lower than those for the entire N = 88 data set ($\bar{x}$ = 3.99% Fe). By excluding the atypical Station 17 data, a higher 3.92% Fe average and a more representative population is established for comparative purposes (Table 25).

Consistent Fe concentrations of 2.12 ± 0.17% were found in the crystal-lattice phase of the N = 12 delta sediment group. These concentrations are essentially the same as those of the river and delta suspended matter (Table 25). The oxidizable fractions are also similar, yet one would expect the sediment value to be higher due to the presence of iron sulfides. SHOKES (1976) found total reduced sulfur in delta sediments to be 0.16 ± 0.09% S. If this low S content is completely combined as FeS_2 or FeS, the associated Fe concentrations would be 0.14 and 0.28% respectively. This expected increase in sediment oxidizable Fe may be obscured by (1) very low

Table 24. Chemical partitioning of metals in Mississippi Delta sediments

Station	Sediment depth (cm)	$CaCO_3$ (%)	Fe (%)					Mn (ppm)						Cu (ppm)					
			Red.	Ox.	Res.	Total (sum)	Total	Exch.	Red.	Ox.	Res.	Total (sum)	Total	Exch.	Red.	Ox.	Res.	Total (sum)	Total
	0-5	0.7	1.12	0.10	1.16	2.38	2.34	84	282	10	95	471	474	0.8	5.3	4.0	8.5	18.6	18.0
17	60-65	0.6	1.50	0.12	1.17	2.79	3.01	127	484	14	103	728	776	<0.2	7.7	5.6	9.3	22.6	23.6
	110-115	1.2	1.49	0.15	1.30	2.94	3.01	63	530	16	106	715	716	<0.2	6.2	3.7	13.1	23.0	24.4
	0-1	0.6	1.72	0.29	1.82	3.83	4.03	94	393	13	118	618	655	0.2	10.6	10.2	9.2	30.2	27.5
12	0-5	0.7	1.63	0.22	1.87	3.72	3.96	77	412	18	117	624	647	<0.2	10.9	9.8	8.6	29.3	32.4
	90-95	0.4	1.89	0.30	1.75	3.94	3.87	132	482	25	105	744	762	<0.2	10.0	6.2	8.9	25.1	31.6
	160-165	0.7	1.72	0.31	1.82	3.84	3.91	80	438	24	108	650	652	<0.2	5.8	7.5	9.2	22.5	29.2
11B	0-1	1.1	1.88	0.21	2.07	4.16	4.15	59	375	20	106	560	576	<0.2	9.4	1.6	16.3	27.3	27.5
	20-25	0.9	1.74	0.37	2.04	4.15	4.12	46	387	23	102	558	559	<0.2	9.4	1.2	-	-	25.2
	50-55	1.1	1.60	0.21	2.04	3.85	3.93	46	450	19	116	631	661	<0.2	3.0	5.9	18.7	27.8	28.1
	90-95	1.9	1.71	0.18	1.86	3.75	3.81	32	572	19	111	734	750	<0.2	3.8	4.7	19.0	27.5	30.3
	0-1	3.4	1.90	0.21	2.10	4.21	4.08	570	1882	28	126	2606	2626	<0.2	12.5	0.7	12.5	25.7	25.9
11A	0-5	3.0	1.67	0.25	2.26	4.18	4.16	26	276	17	105	424	454	<0.2	14.1	1.4	11.7	27.3	26.8
	50-55	1.8	1.35	0.24	2.28	3.87	4.01	26	248	12	109	395	410	0.3	10.1	1.8	12.8	25.0	26.5
	120-125	1.9	1.36	0.20	2.03	3.59	3.64	27	485	18	111	641	669	0.3	1.4	7.7	16.1	25.5	28.2
	Mean N=15		1.62	0.22	1.84	3.68	3.74	66	415	18	108	607	626	<0.2	7.9	5.1	12.5	25.5	27.1
	(std. dev.)		±0.22	±0.07	±0.36	±0.55	±0.53	±35	±97	±4	±6	±113	±116	(-)	±3.7	±3.1	±3.8	±3.1	±3.6
	% of total		44.0	6.0	50.0	100	-	10.9	68.3	3.0	17.8	100	-	-	31.0	20.0	49.0	100	-

(Note: all samples had < 2ppm Exch. Fe)

Table 24 (continued)

Station	Sediment depth (cm)	Ni (ppm) Red.	Ox.	Res.	Total (sum)	Total	Pb (ppm) Red.	Ox.	Res.	Total (sum)	Total	Co (ppm) Red.	Ox.	Res.	Total (sum)	Total
	0-5	11.4	1.2	14.8	27.4	29.2	6.3	4.2	11.4	21.9	22.1	4.3	2.5	4.4	11.2	10.0
17	60-65	14.4	1.2	20.1	35.7	42.4	10.4	5.8	15.1	31.3	31.5	3.6	1.5	5.8	10.9	10.3
	110-115	13.4	0.7	18.5	32.6	40.2	6.6	8.0	16.8	31.4	31.5	4.1	2.4	7.0	13.5	13.8
	0-1	12.7	4.5	23.7	40.9	46.7	11.0	7.1	17.4	35.5	36.4	5.8	1.5	6.8	14.1	14.7
12	0-5	12.8	2.0	24.7	39.5	48.8	12.0	14.1	14.4	40.5	37.9	-	4.9	7.9	-	15.1
	90-95	12.4	2.7	23.5	38.6	42.6	11.7	-	17.3	-	40.5	-	1.8	8.0	-	13.7
	160-165	11.4	2.2	23.9	37.5	42.1	15.7	5.8	9.9	31.4	31.1	7.1	0.9	6.1	14.1	15.0
	0-1	14.8	6.0	27.8	48.6	54.9	15.4	17.6	16.4	49.4	-	5.2	4.3	8.3	17.8	15.3
11B	20-25	15.2	5.2	24.6	45.0	53.2	13.9	12.9	15.7	42.5	45.2	6.7	3.7	8.8	19.2	15.5
	50-55	8.9	6.3	25.8	41.0	44.0	7.6	9.4	17.1	34.1	29.2	6.9	4.4	8.0	19.3	15.2
	90-95	11.9	2.4	23.0	37.3	43.9	14.0	4.6	17.6	36.2	32.3	4.3	4.7	8.4	17.4	14.2
	0-1	12.6	2.8	24.9	40.3	40.6	15.8	1.5	17.0	34.3	38.8	7.1	1.5	7.3	15.9	15.3
11A	0-5	13.5	4.3	24.2	42.0	43.2	16.3	-	12.8	-	35.5	4.3	2.0	8.9	15.2	14.8
	50-55	11.9	1.1	26.6	39.6	38.1	6.8	7.5	13.4	27.7	22.8	4.6	1.3	9.4	15.3	11.2
	120-125	9.5	3.0	21.7	34.2	34.6	5.2	2.2	17.1	24.5	22.0	5.5	2.9	8.5	16.9	13.0
	Mean	12.5	3.0	23.2	38.7	43.0	11.2	7.7	15.3	33.9	32.6	5.3	2.7	7.6	15.4	13.8
	(std. dev.)	±1.8	±1.8	±3.3	±5.1	±6.5	±3.9	±4.7	±2.4	±7.4	±7.0	±1.3	±1.4	±1.4	±2.7	±1.9
	% of total	32.3	7.8	59.9	*100*	-	32.8	22.5	44.7	-	-	34.0	17.3	48.7	-	-

(Note: all samples had < 0.5 ppm Exch. Ni, Pb and Co)

Table 25. Comparison of chemical partitioning of metals in Mississippi River and Delta suspended matter and Mississippi Delta sediments

		Fe (%)				Mn (ppm)					Cu (ppm)				
		Red.	Ox.	Res.	Total (sum)	Exch.	Red.	Ox.	Res.	Total (sum)	Exch.	Red.	Ox.	Res.	Total (sum)
River suspended matter	Mean (N=12)	2.37	0.28	1.96	4.61	118	1180	31	105	1428	0.7	16.9	12.7	14.0	44.3
	% of total	51.4	6.1	42.5	100	8.2	82.3	2.2	7.3	100	1.6	38.1	28.7	31.6	100
River delta suspended matter	Mean (N=19)	2.21	0.31	2.01	4.53	173	950	32	105	1260	2.2	24.8	13.2	14.4	54.6
	% of total	48.8	6.8	44.4	100	13.7	75.4	2.6	8.3	100	4.0	45.4	24.2	26.4	100
Nearshore GOM sediments*	Mean (N=12)	1.77	0.26	2.12	4.15	61	436	19	117	633	(<0.2)	8.9	5.5	13.8	28.2
	% of total	42.6	6.3	51.1	100	9.6	68.9	3.0	18.5	100	-	31.6	19.5	48.9	100

		Ni (ppm)				Pb (ppm)				Co (ppm)			
		Red.	Ox.	Res.	Total (sum)	Red.	Ox.	Res.	Total (sum)	Red.	Ox.	Res.	Total (sum)
River suspended matter	Mean (N=12)	23.5	3.5	28.5	55.5	20.3	14.4	14.8	49.5	8.8	4.6	8.1	21.5
	% of total	42.3	6.3	51.4	100	41.0	29.1	29.9	100	40.9	21.4	37.7	100
River delta suspended matter	Mean (N=19)	21.2	3.5	28.4	53.1	25.2	18.4	16.8	60.4	7.4	4.7	8.2	20.3
	% of total	39.9	6.6	53.5	100	41.7	30.5	27.8	100	36.4	23.2	40.4	100
Nearshore GOM sediments*	Mean (N=12)	13.0	3.8	26.0	42.8	12.8	8.8	16.4	38.0	6.1	3.0	8.5	17.6
	% of total	30.4	8.9	60.7	100	33.7	23.1	43.2	100	34.7	17.0	48.3	100

* Data set does not include Station 17 and concentrations are given salt-free, $CaCO_3$-free.

reduced S in the sediments leached, (2) a smaller carry-over of oxide-phase Fe during leaching of the sediments relative to the suspended matter or (3) incomplete removal of the sulfide phase. Delta sediment total Fe concentrations are about 8% lower than those for river suspended matter. This significant difference is the result of a 25% decrease in the oxide fraction (from 2.3% to 1.77%). Because the Fe loss is restricted to the reducible phase, it suggests either that some of the Fe coating has been lost by a reduction-diffusion process or that sediment with more Fe-rich coatings has by-passed the delta. Another possibility is that some of the original oxide-phase Fe has become less susceptible to reduction by dithionite.

Total sediment Mn concentrations are 41% lower than those for river particulates (Table 25). This percentage decrease is somewhat exaggerated (56%) in the leach samples studied (Table 24). Suspended matter and sediment lattice-held Mn concentrations are similar at 105 and 117 ppm respectively. Even the Mn-rich surface sediment from Station 11A (2626 ppm total Mn) has a comparable 126 ppm residual Mn. This points out the basically similar mineralogy of these continental weathering products. Exchangeable Mn concentrations in delta sediments are lower than suspended particulate values (Table 25), probably as a function of the decreased organic fraction and the reduced Mn oxide content.

Mn-oxide coatings on the deposited sedimentary material are markedly lower than those of the river particulates (436 ppm vs. 1180 ppm). The reducible phase again accounts for most of the decrease in total metal concentrations. This observation supports either a chemical or a physical fractionation of metal oxides. Data from Station 11A (Table 24), however, support chemical fractionation of Mn. The surface centimeter of sediment at Station 11A has higher reducible Mn (1882 ppm) than any other delta sediment or suspended matter sample, yet the subsurface samples have lower reducible Mn concentrations (260 ppm) than any other sample. These changes occur even though Station 11A Al concentrations are constant. Such observations have been made many times (e.g. LYNN and BONATTI, 1965). Of greater significance is the absence of Mn-rich layers at Stations 17, 12 or 11B even though the river suspended material has almost 3 times higher reducible Mn than these sediments. This distinction will be addressed in the subsequent interstitial water presentation.

Analogous to Mn, nearshore sediment total Cu concentrations (for the N = 12 subgroup) are 36% lower than those for river suspended matter, yet average lattice Cu concentrations are the same at 13.8 and 14.0 ppm. Sediment reducible and oxidizable Cu concentrations are each about one-half the river particulate values. This again shows a decrease in the surface metal coating of the delta sediments relative to the suspended matter. Virtually no exchangeable Cu was found in the delta sediment.

Nickel partitioning in the delta sediments parallels that of Fe,

Mn and Cu. Residual and oxidizable Ni concentrations in the sediments are statistically the same as those in the river and delta suspended matter. Sediment reducible Ni concentrations, however, are 45% lower than particulate values.

Lead partitioning is somewhat distorted by pollution. Residual concentrations in the suspended particulates and nearshore sediments are alike (Table 25). however, average reducible and oxidizable Pb concentrations are lower in the sediments because pollutant Pb inputs are less in deeper sediment layers.

Lattice-held Co concentrations for delta sediments (8.5 ppm) are equivalent to those of the suspended matter (Table 25). Sediment reducible and oxidizable values are 25 and 35% lower respectively than those of the particulates (Table 25), however the absolute differences are small (2.0 and 1.6 ppm respectively). Although these data suggest loss of Co from delta sediments, similar to that observed for Fe, Mn, Cu and Ni, the evidence is less definitive.

Interstitial Water

Lower Mn, Ni, Cu, Co and Fe oxide-phase concentrations in Mississippi Delta sediments relative to Mississippi River particulates may be due to a diffusive loss of reduced species from the sediment interstitial water to the overlying seawater. To assess the quantitative importance of post-depositional metal fluxes, interstitial water Fe and Mn gradients in delta sediments were determined.

The present work is a continuation of a long-term Mississippi Delta interstitial water program by our group at Texas A&M University (ARMSTRONG, 1974; SHOKES, 1976; and unpub. data). Previous interstitial water data from 33 delta cores (Fig. 24) show some of the basic trends observed and thus are reviewed below.

Sulfate reduction is found over the entire delta area, with the extent or rate of reduction decreasing seaward of the river mouth. Alkalinity and ammonia generally show corresponding increases with depth for these anoxic nearshore sediments. Phosphate profiles are varied, some showing steady decreases with sediment depth whereas others increase to a subsurface maximum and then decrease, suggesting that other factors besides organic decomposition (e.g. inorganic precipitation or adsorption) are influencing phosphate behavior.

Interstitial Fe and Mn concentrations (Table 26) were also determined for the 33 cores studied during this initial pore water work. Pore water Mn concentrations ranged from 0.2 to 27 mg/ℓ, averaging 4.4 mg/ℓ and Fe values ranged from <0.05 to 107 mg/ℓ, averaging 4.5 mg/ℓ. Interstitial Mn and Fe concentrations generally decrease seaward of the Mississippi River mouth (Fig. 24 and Table 26) as a function of decreasing sedimentation rate (i.e. rate and extent of sulfate reduction, see SHOKES, 1976). Maximum interstitial Mn concentrations were found in the surface sediment samples (0-10 cm) 90% of the time. Maximum pore water Fe concentrations, however, were found in surface sediments in only 30% of the cores studied. In fact, the topmost sediment interstitial Fe values were often quite low (<0.05 mg/ℓ), particularly in areas of low sedimentation rate.

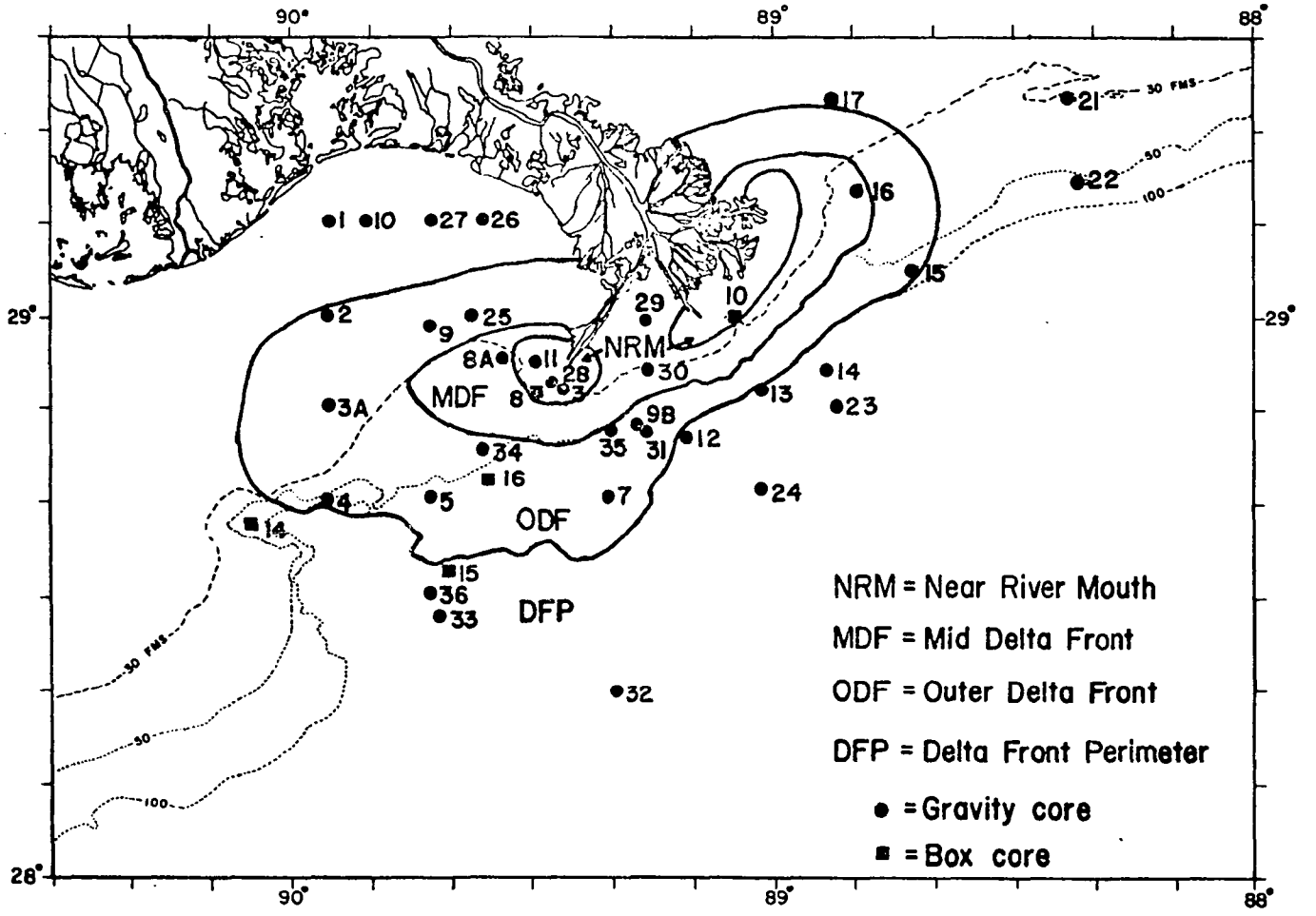


Fig. 24. Mississippi Delta interstitial water sampling sites.

Table 26. Mississippi Delta interstitial water Mn and Fe summary

Location	No. of cores	No. of samples	Sed. rate † ($g\ cm^{-2}y^{-1}$)	Interstitial Water			
				Mn		Fe	
				Mean (mg/ℓ)	Max.* (mg/ℓ)	Mean (mg/ℓ)	Max.* (mg/ℓ)
Near River Mouth (NRM)	3	12	> 3	9.1	20.2	29.4	75.0
Mid-Delta Front (MDF)	5	20	1.5	6.6	14.7	4.9	11.3
Outer-Delta Front (ODF)	9	36	0.8	4.5	7.8	1.3	2.2
Delta-Front Perimeter (DFP)	16	61	<0.5	2.6	4.1	2.4	5.9

† Data from SHOKES (1976).

* Mean value for maximums in all cores from specified location.

Where interstitial Fe concentrations were high, copious amounts of a red iron oxide precipitated in the squeezed, filtered water. In no case was a significant amount of Mn precipitated. This difference in behavior was determined by analyzing an aliquot of pore water before and after acidification. For example, prior to acidification a sample might have 0.2 mg/ℓ Fe and 12.0 mg/ℓ Mn whereas after dissolving the precipitate, corrected values were 16.6 mg/ℓ Fe and 12.6 mg/ℓ Mn. These observations support the more easily facilitated precipitation of iron oxides and the preferential precipitation of Mn^{2+} only at surfaces (e.g. clays) where substantial kinetic barriers are overcome by catalysis (MANHEIM, 1976). Note, however, that iron oxides do not provide a conducive surface for Mn precipitation in this case.

Selected profiles of interstitial Fe, Mn, SO_4^{2-}, NH_4^+, PO_4^{3-}, and alklinity from the Texas A&M work (Fig. 25) show differences in species distribution for the major sediment regimes of the Mississippi Delta (Fig. 24). Although these interstitial water profiles are not complete enough to allow thorough description, they outline some of the generally reported diagenetic trends. For example, Figs. 25a-e show the commonly observed delta case where sulfate reduction with corresponding increases in ammonia, alkalinity and phosphate occur. This may be represented in a generalized reaction for organic decomposition under anaerobic conditions:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} = 106HCO_3 + 53HS^- + 16NH_4^+ + HPO_4^{2-} + 39H^+ \quad (3)$$

Figs. 25a, c and d also show the high interstitial Mn concentrations in delta surface sediments. Manganese concentrations decrease

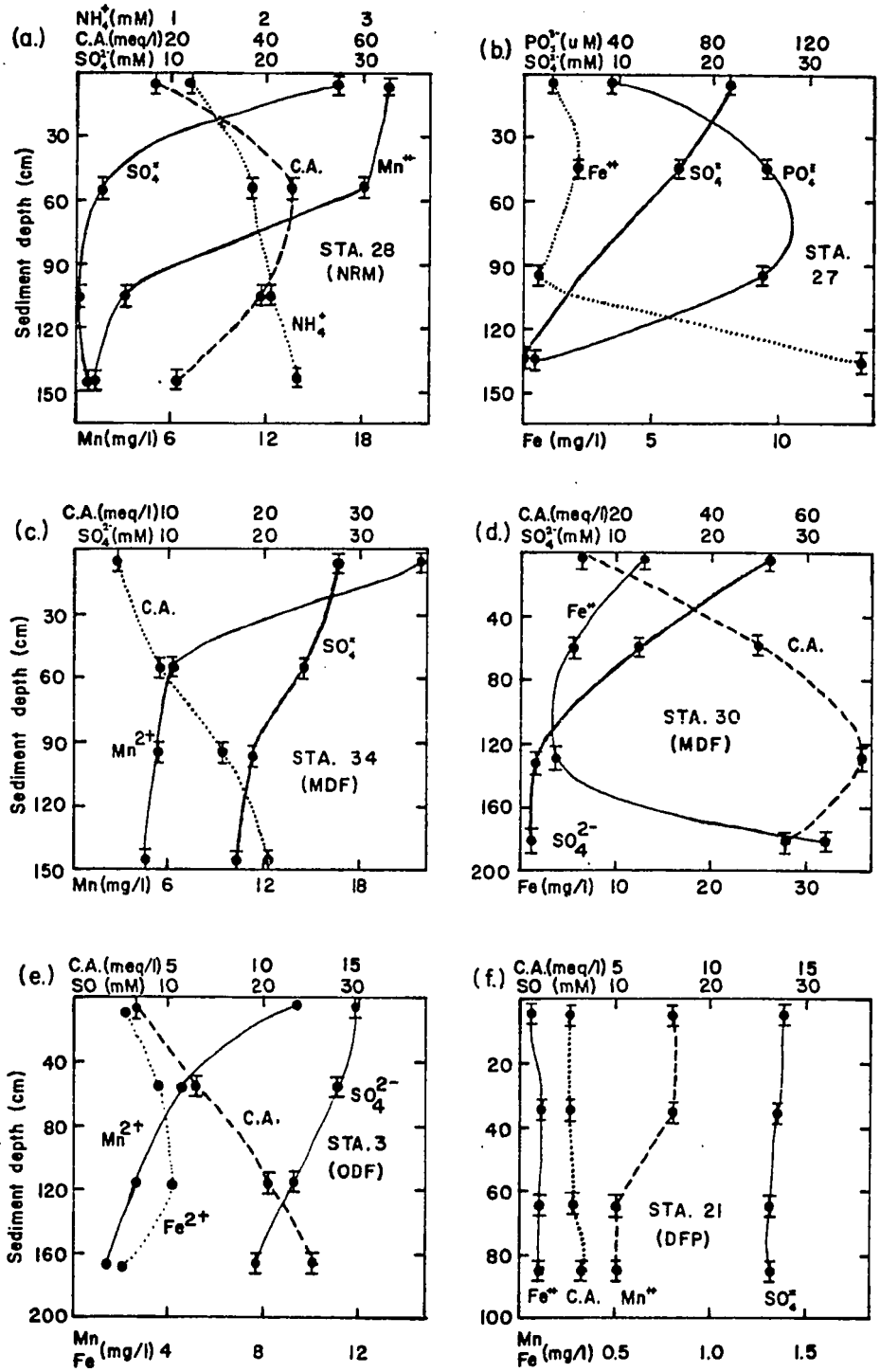


Fig. 25. a-f. Interstitial water profiles for selected species at various Mississippi Delta sampling sites (C.A. = carbonate alkalinity).

with sediment depth and increasing carbonate alkalinity (C.A) as the K_{sp} of rhodocrosite ($MnCO_3$) is exceeded (ROBBINS and CALLENDER, 1975; HOLDREN et al., 1975). In slowly accumulating, oxygenated, Station 21 sediment (Fig. 25f), Fe and Mn are in low concentrations and show no marked variation with depth. It was not the immediate purpose of this work to model the observed behavior of Fe and Mn, however, an awareness of the above factors in considering diffusive fluxes of Mn and Fe from the various delta environments is helpful.

As part of the present work, Mn and Fe concentrations were determined for interstitial water and sediment at four delta locations. Fig. 26 shows the Mn and Fe profiles for near river mouth Station 8 (Fig. 24). The sediment accumulation rate at this site is on the order of 2 g $cm^{-2}y^{-1}$ as estimated by the interstitial dissolved sulfate profile (SHOKES, 1976). Total Mn concentrations in Station 8 sediment are relatively constant at 686 ppm ($CaCO_3$-free, salt-free) with slightly higher values in the 10-20 cm section. No surficial Mn-rich layer was found at Station 8 and the Mn/Al ratio for these sediments (84×10^{-4}) is 44% lower than that for the river particulates (150×10^{-4}). Mn-oxide coatings account for ∿70% of the total sediment Mn at Station 8 and the Mn concentration of the lattice fraction is constant at ∿110 ppm.

The flux of Mn in particulate form (F_{Mn}) to the sediment column may be determined by:

$$F_{Mn} = [Mn]_p \, s \qquad (4)$$

where $[Mn]_p$ = the concentration of Mn in the river particulates (1300 µg Mn/g) multiplied by the sediment/river-particulate Al ratio

s = sediment accumulation rate (g $cm^{-2}y^{-1}$)

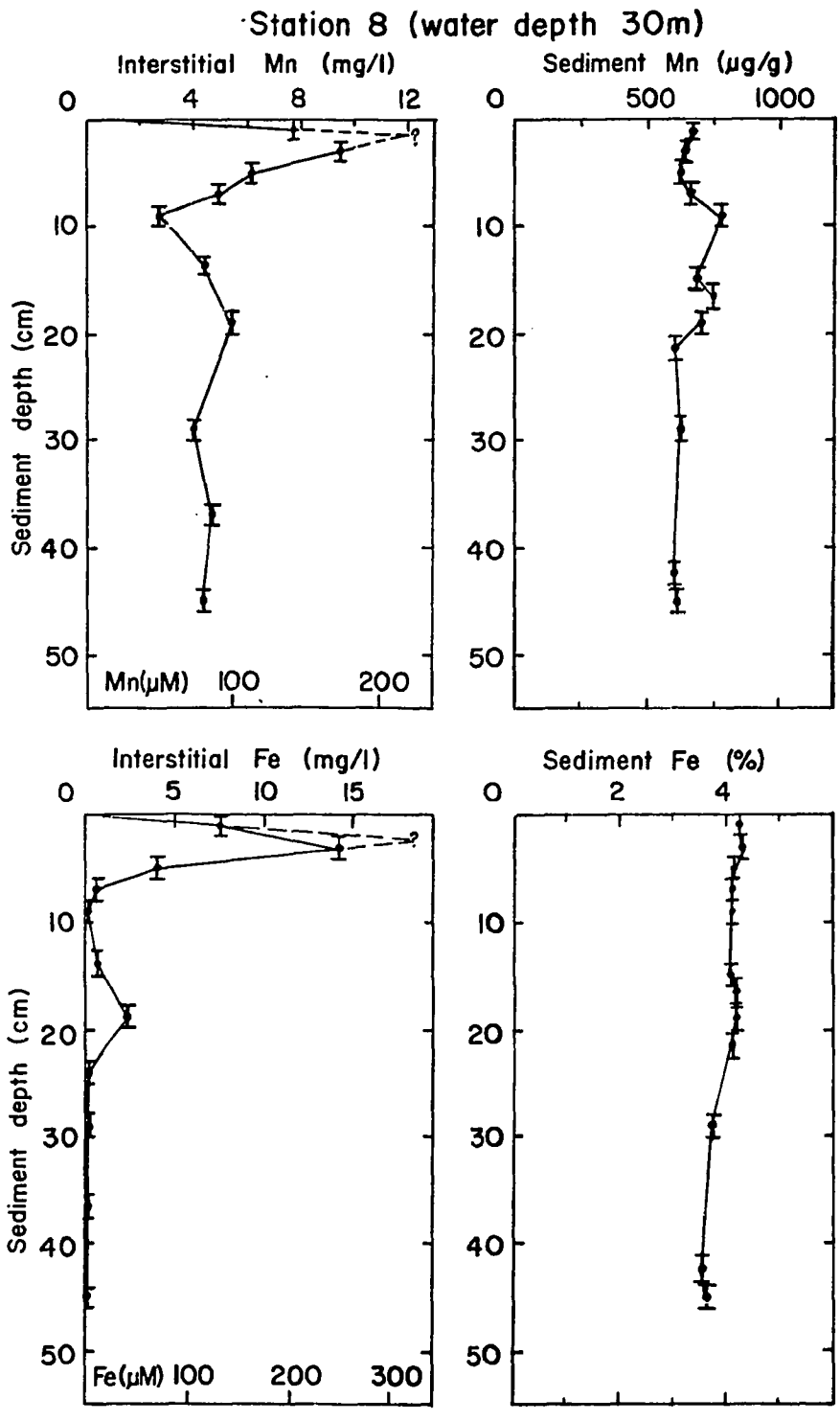


Fig. 26. Interstitial water and sediment Mn and Fe profiles for Station 8.

and is equal to ∿2460 μg Mn cm^{-2} y^{-1} at Station 8. The net accumulation rate of Mn ($F_{Mn,\ net}$) at Station 8, (based on the average sediment Mn concentration of 686 ppm) however, is ∿1370 μg Mn cm^{-2} y^{-1}, almost one-half of that expected from the incoming Mn flux.

The interstitial water Mn profile at Station 8 (Fig. 26) shows a sharp gradient with the 0-2 cm section having a concentration of 8 μg Mn/cm^3. The diffusive flux of Mn from these sediments may be calculated by Fick's first law (equation 2, p. 9).

$$F_{Mn}^{2+} = -D_s \frac{dc}{dx} \qquad (2)$$

where D_s = molecular diffusion coefficient, corrected for porosity and tortuosity (cm^2/y)

$\frac{dc}{dx}$ = the concentration gradient for Mn (μg cm^{-3} cm^{-1})

LI and GREGORY (1974) show that the corrected interstitial water diffusion coefficient (D_s) may be obtained from the aqueous molecular diffusion coefficient (D_m) by

$$D_s = \phi\ D_m/\theta^2 \qquad (5)$$

where ϕ = porosity (interstitial water volume fraction)

θ = tortuosity (ratio of diffusion path length to straight path distance)

and give a D_m value for Mn^{2+} of 3.05 x 10^{-6} cm^2/sec at 0°C. The sediment/interstitial water temperature at Station 8 (water depth 30 m) was measured immediately upon retrieval of the core and found

to be 21°C. LI and GREGORY (1974) show that the diffusion coefficient for Mn^{2+} may be corrected for temperature by the Stokes-Einstein relation,

$$\left(\frac{D_m\, n}{T}\right)_{T_1} = \left(\frac{D_m\, n}{T}\right)_{T_2} \qquad (6)$$

where n = the viscosity of seawater (centipoises) at a given temperature, T (°K).

Using sea water viscosities (RILEY and SKIRROW, 1975, p. 618), D_m for Mn^{2+} at 21°C is equal to 5.9×10^{-6} cm^2/sec.

Substituting the porosity at Station 8 (0.77) and a tortuosity value of 1.15 (VAN BRAKEL and HEERJES, 1974) into equation (5), D_S equals 3.5×10^{-6} cm^2/sec (110 cm^2/y). Using a gradient of 9 µg Mn cm^{-3} cm^{-1} (from Fig. 26) the net diffusive flux from Station 8 sediments to the overlying water (from Eq. 2) is ∿1000 µg Mn cm^{-2} y^{-1}, in agreement with the projected loss.

The interstitial water Mn gradient and the sedimentation rate at Station 8 are not completely defined. Neither are the effects of bioturbation and bottom currents in this shallow delta environment. Nevertheless the available data do support a reduction-diffusion mechanism for Mn loss from these sediments. Solubilized Mn species are most likely adsorbed and subsequently oxidized on the surfaces of the abundant particulates which are being actively carried away from the delta area.

Iron behavior at Station 8 may be treated similarly. Sediment Fe concentrations average 4.17 ±0.30% ($CaCO_3$-free, salt-free) with the top 18 cm having an Fe/Al ratio of 0.526, in good agreement with the river particulates. The bottom 18 cm at Station 8 had a lower Fe/Al

ratio (0.488). Station 8 Al concentrations average 8.17 ± 0.33% ($CaCO_3$-free, salt-free) which is ∿6% lower than those for the river particulates and may be due to some river bedload input or physical sorting of particles.

The incoming flux of Fe (F_{Fe}) is equal to 88 mg $cm^{-2}y^{-1}$ and the net accumulation rate ($F_{Fe,net}$) is 87 mg Fe cm^{-2} y^{-1}. Using the calculated D_s for Fe (at 21°C) of 3.9 x 10^{-6} cm^2/sec (122 cm^2/y) (LI and GREGORY, 1974) and $\frac{dc}{dx}$ = 8 µg cm^{-3} cm^{-1}, the diffusive flux from Station 8 sediments to the overlying water is ∿1 mg Fe cm^{-2} y^{-1}. The agreement between the diffusive flux and inferred loss is again close. This is somewhat surprising in view of the uncertainty in some of the variables. Nevertheless, the evidence for Mn and Fe diffusion from Station 8 sediments is quite good. These field observations are supported by the experiments of GRAHAM et al. (1976) who measured a benthic Mn flux of ∿700 µg cm^{-2} y^{-1}.

Other trace metals have not yet been measured in the delta interstitial waters. It would be pure speculation to consider reduction-diffusion as a mechanism for removing other metals from the nearshore sediments. However, at Station 8, where D_s for Cu (at 21°C) is 3.9 x $10^{-6}$$cm^2$/sec (122 cm^2/y, LI and GREGORY, 1974), a gradient for Cu of 0.2 µg cm^{-3} cm^{-1} would be sufficient to account for the decrease in sediment concentrations (32 µg Cu/g) relative to the river particulates (43 µg/g). This would mean that interstitial Cu concentrations would have to be on the order of 200 µg/ℓ in the surface centimeters of sediment. Similar behavior may also be postulated for Co, Ni and Zn.

A sizeable flux of Fe and Mn diffuses from the delta sediments to the overlying water. This is shown by the absence of any surface Mn-rich zone in the Near River Mouth and Mid-Delta Front sediments (Fig. 24) from Stations 17, 8, 10, 12, and 11B, and the interstitial gradients measured. In Outer Delta Front and deeper water sites (>100 m, water depth), however, there are measurable Mn-rich zones (Fig. 27). Manganese-rich zones have also been observed by MCKEE (1977) and HOLMES (1976) in northern Gulf of Mexico slope sediments. MCKEE found that the thickness of the oxidized-sediment layer and hence the depth of the metal-rich zone generally increased with water depth (i.e. decreasing sedimentation rate). He also observed near-surface maxima in interstitial Mn with smaller, deeper Fe maxima, and used these data to restate the differential redox behavior of the two metals previously noted by KRAUSKOPF (1957).

Data from this work for outer delta Station 16 (Fig. 27b) show that the top 2 cm of the sediment are enriched in Mn (1860 µg/g) whereas the rest of the sediment column is depleted in Mn (660 µg/g) relative to the Mississippi River particulates. Chemical partitioning data (Table 24 p. 117), has shown that the bulk of the Mn is in the oxide phase and that concentration changes, such as observed for Station 16, are due to changes in the Mn oxide content of the sediment.

The incoming particulate flux of Mn at Station 16 is 688 µg cm^{-2} y^{-1} (1368 µg Mn/g x 0.5 g sediment cm^{-2} y^{-1}) and the net Mn accumulation rate is 330 µg cm^{-2} y^{-1} (660 µg Mn/g x 0.5 g cm^{-2} y^{-1}). This implies that 358 µg Mn cm^{-2} y^{-1} are being lost to the Mn-rich

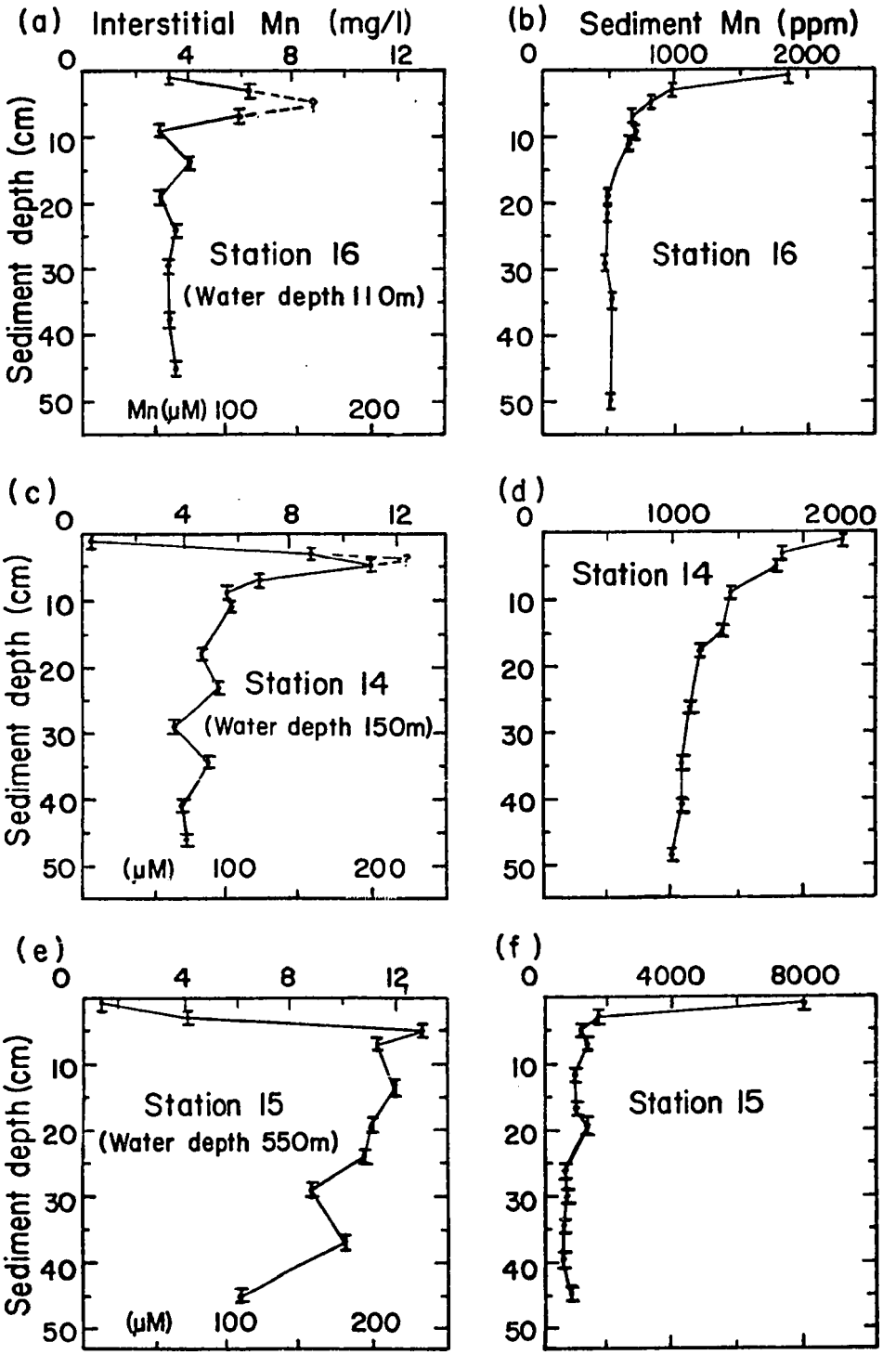


Fig. 27. a-f. Interstitial water and sediment Mn profiles for Station 16, 14 and 15.

zone and/or the overlying seawater. However, the total excess Mn at Station 16 (all of which is in the surface 2 cm, Fig. 27b) is only about 1000 μg/cm^2. Thus, even at this outer delta station, much of the diagenetic Mn is either diffusing to overlying seawater or accumulating in the surface millimeters of sediment and being winnowed away.

Sedimentation rates at outer delta Stations 14 and 15 (Fig. 24) are 0.35 and 0.08 g cm^{-2}y^{-1} respectively. Figs. 27d and f show that the depth and magnitude of the Mn-rich zone in these sediments has increased relative to nearshore areas. Pertinent Mn flux data for Stations 14 and 15 are given below (all fluxes are given in μg cm^{-2} y^{-1}).

	F_{Mn}	$F_{Mn,\ net}$	D_s (cm^{2}y^{-1})	$F_{Mn^{2+}}$	Upward flux of Mn-rich zone
Station 14	480	385	94	320	280
Station 15	116	84	82	260	330

At Station 14 about 95 μg Mn cm^{-2}y^{-1} of the incoming flux (F_{Mn}) are not buried at depth in the sediment column. This remobilized Mn has left an accumulated excess of 3000 μg Mn/cm^2 in the surficial sediments (Fig. 27d). The upward flux of dissolved Mn ($F_{Mn^{2+}}$) at Station 14 supports the upward movement of this Mn-excess zone. Any additional flux of dissolved Mn may add to the surface excess or diffuse from the sediments.

At Station 15, the rate of loss of Mn (32 μg cm^{-2} y^{-1}) is small relative to the 10,000 μg Mn/cm^2 excess in the top 4 cm of sediment. This implies a more lengthy time interval for the formation of the Mn excess. Furthermore, the $F_{Mn^{2+}}$ at Station 15 is insufficient to account for the upward migration of the Mn-rich zone. Certainly most of the Mn flux to Station 15 is staying within the sediment column. Interstitial

Fe concentrations were low at Stations 14, 15 and 16 (<50 µg/ℓ) and thus no significant flux of Fe from these sediments occurs.

In summary, the interstitial water data support a reduction-diffusion mechanism for Mn (and Fe) loss from nearshore sediments. This process is most efficient where delta sediments accumulate at >0.5 g cm^{-2} y^{-1}. Particles transported over the delta to deeper waters may progressively adsorb remobilized Mn and bring a higher particulate Mn flux to outer delta areas. Where sedimentation rates are <0.5 g cm^{-2} y^{-1} a measurable Mn-rich zone is formed by subsurface remobilization and surface precipitation of Mn. In some cases, a flux of dissolved Mn to the overlying seawater may still occur. Bottom currents may also winnow away surface Mn-rich layers throughout the delta and slope areas. The above processes all direct an enriched Mn flux to deep Gulf sediments.

Deep Gulf of Mexico Sediments

Table 27 summarizes metal, carbonate and grain size values for deep Gulf of Mexico sediments (Fig. 28); the complete data set is given in APPENDIX E. Variations in concentrations and changes within a given core are sometimes considerable and reflect differences in depositional environment and sedimentation rate. These variations will be considered in separate discussions of each core.

Comparison of overall mean values from this study with those of previous investigators (Table 28) shows generally good agreement among Fe, Al, Mn, Zn, Pb, Cu, Cr, and V, considering variations in $CaCO_3$

Table 27. Gulf of Mexico sediment metal, $CaCO_3$ and grain size distribution

Station	N	Water depth (m)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	$CaCO_3$ (%)	Silt (%)	Clay (%)
24	9	1150	3.47 (±0.23)	7.34 (±0.19)	4700* (-)	103 (±3)	16.8 (±1.1)	28.1 (±2.1)	14.4 (±1.4)	72 (±11)	50.3 (±6.8)	0.3 (±0.1)	152 (±16)	15.1 (±2.7)	30.3 (±5.3)	67.0 (±5.3)
10A, 9	2	2680 2960	2.12	5.02	1060	66	15.7	26.4	10.4	42	35.3	-	-	39.2	-	-
4	9	2710	3.60 (±0.49)	7.72 (±0.49)	975* (±511)	101 (±13)	17.6 (±3.4)	35.6 (±6.4)	20.0 (±8.3)	-	42.1 (±9.2)	0.1 (-)	181 (±53)	10.9 (±9.2)	28.7 (±2.7)	67.7 (±8.0)
5	11	3350	3.50 (±0.62)	7.46 (±1.12)	1620* (±110)	99 (±15)	18.1 (±2.7)	44.8 (±12.3)	20.7 (±4.7)	62 (±11)	46.9 (±6.6)	0.1 (-)	179 (±26)	16.5 (±10.4)	21.0 (±5.3)	71.2 (±16.4)
6	14	3400	2.71 (±0.45)	5.93 (±0.73)	2450* (±1840)	78 (±14)	16.3 (±2.6)	46.7 (±11.1)	21.2 (±13.2)	45 (±15)	54.6 (±12.3)	0.3 (±0.1)	98 (±19)	36.1 (±6.4)	20.6 (±12.9)	43.6 (±4.7)
Mississippi Delta Sediments (N = 88)			3.99 (±0.37)	8.11 (±0.58)	743 (-)	125 (±13)	34 (±8)	28 (±4)	15 (±2)	84 (±12)	41 (±5)	0.8 (±0.5)	141 (±17)	1.1 (±0.8)	36.6 (±7.7)	60.2 (±14.2)
Mississippi River Particulates (N = 43)			4.61 (±0.40)	8.65 (±0.70)	1300 (±180)	193 (±23)	46 (±6)	45 (±7)	21 (±2)	79 (±3)	55 (±4)	1.3 (±0.4)	150 (-)	- -	40.8 (±8.7)	59.0 (±8.7)

* Data set includes surface and/or subsurface Mn enrichment.

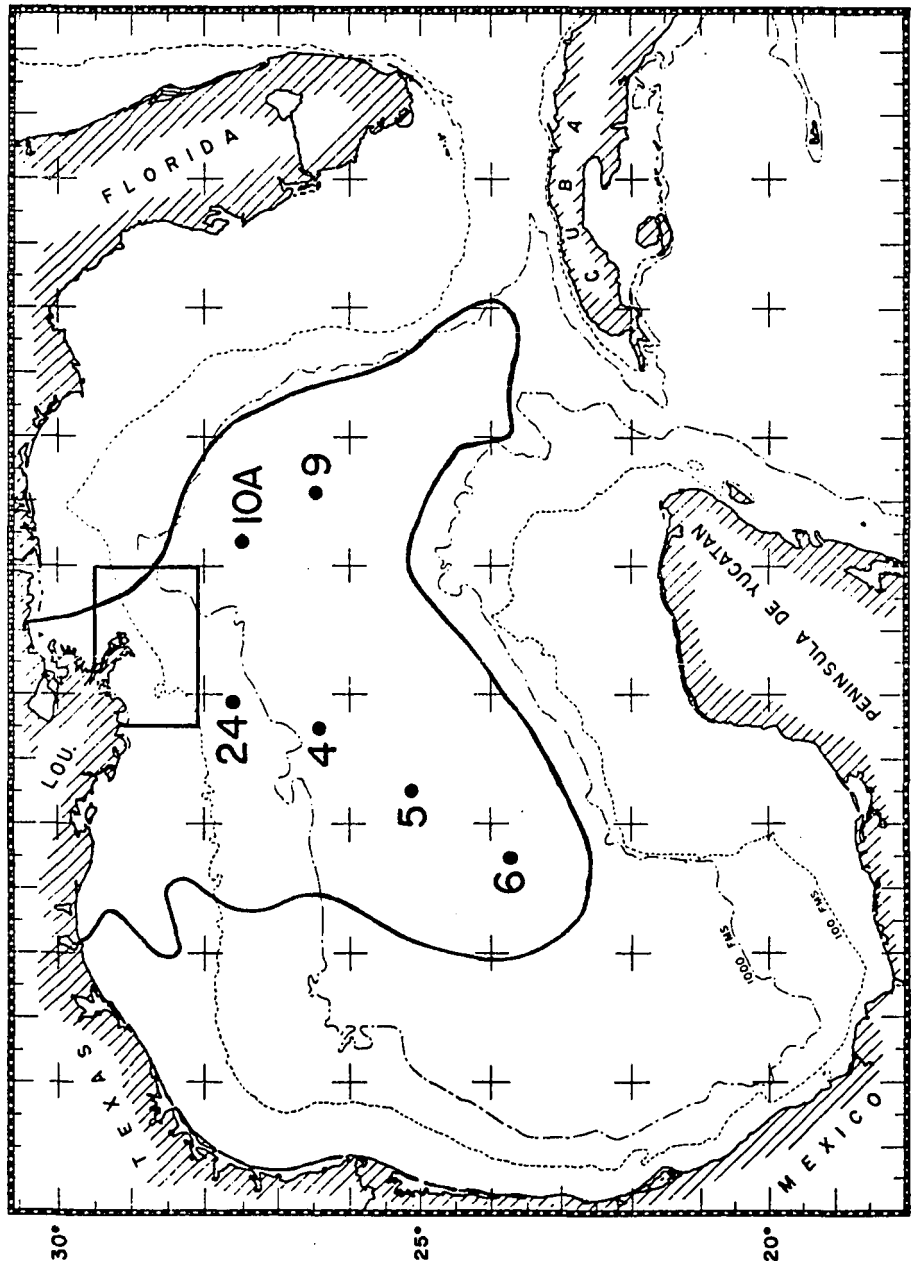


Fig. 28. Deep Gulf of Mexico sediment sampling sites.

Table 28. Reported metal concentrations for Gulf of Mexico sediments

	No. of samples	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	V (ppm)	Cd (ppm)	$CaCO_3$ (%)
Lower Miss. Fan (HOLMES and HEARN, 1942)	2	4.24	8.06	900	-	-	-	-	-	-	-	-	-
Slope, rise, plain (TRASK, 1953)	8	3.4	7.4	-	-	-	-	-	-	-	-	-	-
Lower Miss. Fan (YOUNG, 1954)	6	-	-	-	-	-	-	20	90	53	144	-	~10
Slope, rise, plain, knolls (WATSON and ANGINO, 1969)	104	3.12	-	1600	-	-	-	40	-	115	-	-	28
"Yellow" layers (WATSON and ANGINO, 1969)	26	5.17	-	2100	-	-	-	60	-	150	-	-	26
Plain and knolls (TIEH and PYLE, 1972)	32	2.86	-	1850	72	-	-	-	-	84	-	-	14
Slope, rise, plain, lower Miss. Fan (HOLMES, 1976)	2482	2.46	-	900	-	11	23	20	84	40	133	-	11
Slope, rise, plain, knolls (This study)	43	3.25	6.95	1870	94	17	40	19	57	50	146	0.2	22
Deep-sea clay (CHESTER and ASTON, 1976)	-	6.50	-	6700	165	80	250	74	90	225	120	0.2	-

content and sample locations. Lower Mn values determined by HOLMES and HEARN (1942) and HOLMES (1976) are biased by a predominance of turbidite sequence and slope samples. High Ni and Co values found by WATSON and ANGINO (1969) for normal gray lutite may be an artifact of analytical methodology, namely that no correction for molecular absorbance due to Fe and $CaCO_3$ was made (see APPENDIX B). Certainly the central Gulf of Mexico is not characterized by metal-rich pelagic clays to the extent found in the slowly accumulating sediments of the Atlantic and Pacific Oceans. Possible exceptions to this generalization are Gulf "yellow" layers, ironstones and Sigsbee Knoll sediments.

Continental slope sediment from Station 24 (Fig. 29) is characterized by a relatively uniform 15% $CaCO_3$ and 67% clay (<2 μm particles) and a 10 cm Mn-rich oxidized zone (Fig. 29, Table 25 and APPENDIX E). Grain size determinations for Station 24 sediment treated with acetate buffer to remove $CaCO_3$ yielded 77% clay, with two-thirds of the clay-size particles (50% of the total $CaCO_3$-free sediment) <0.5 μm in size (see APPENDIX F). The above values differ somewhat from those for nearshore sediments which have ∿1% $CaCO_3$, 60% clay (with 40% of total sediment <0.5 μm) and very thin (1-5 cm) or non-existent Mn-rich zones. The sediment accumulation rate for Station 24 is about 60 g cm^{-2} $10^{-3}y^{-1}$ (SHOKES, unpublished data), again distinct from nearshore sedimentation rates of 100 to >3000 g cm^{-2} $10^{-3}y^{-1}$.

Fig. 29 shows that metal concentrations (except for Mn) are uniform with depth over the estimated 1500 year history of this

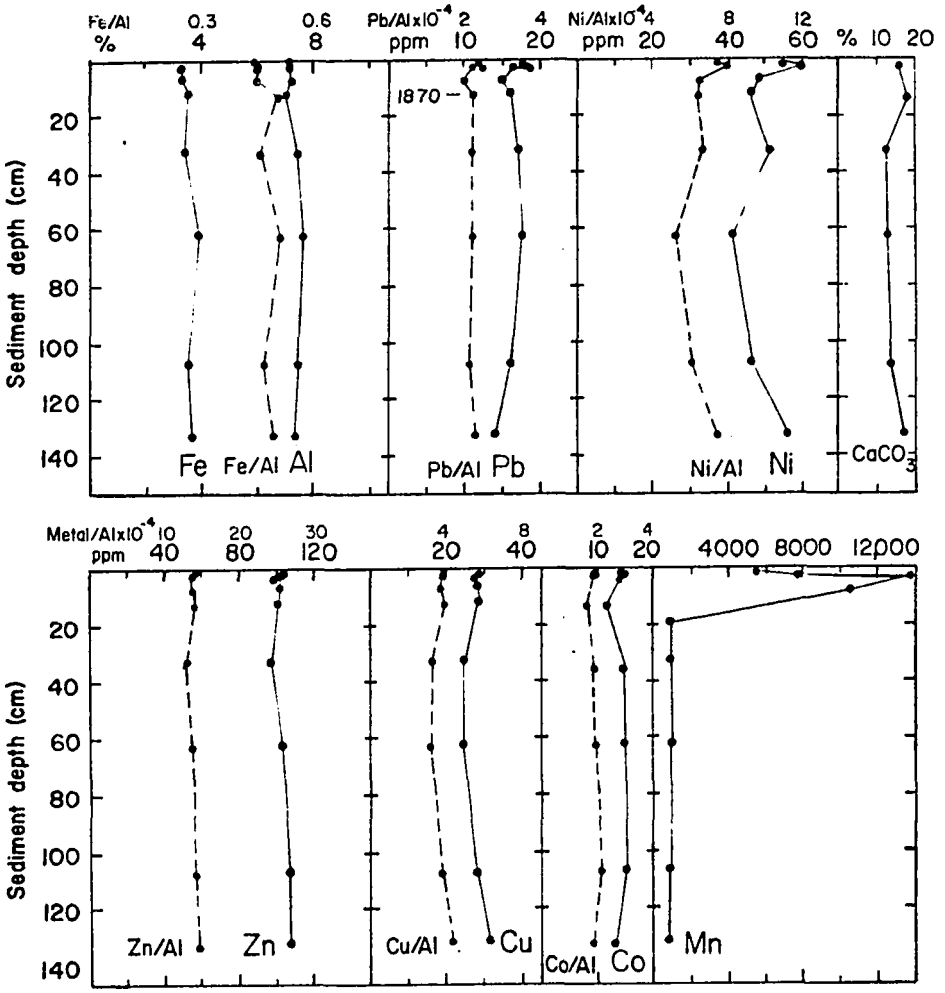


Fig. 29. Vertical metal and $CaCO_3$ profiles for Station 24 sediment (water depth 1150 m). Dates based on Pb-210 geochronologies (SHOKES, unpub. data).

slope core. Iron, Zn, Co and Cr concentrations for Station 24 ($CaCO_3$-free, salt-free) are comparable to those for delta sediments (Table 27) and river particulates, whereas Al values are ∿7% higher. Average Cu, Co and Ni concentrations ($CaCO_3$-free, salt-free) are 15-30% higher than found in nearshore sediments, yet are comparable to or lower than those for river particulates. Thus, despite a 30% increase in clay content, there is no evidence of any overall metal enrichment which might be related to particle size. Furthermore, the sediment accumulation rate (60 g cm^{-2} 10^{-3} y^{-1}) would not be conducive to significant chemical deposition of metals at this site.

Although most metals have uniform and predictable metal concentrations at Station 24, the Mn profile (Fig. 29) is characterized by high surface sediment values (>5000 ppm) which increase to a maximum of ∿15,000 ppm at 5 cm and then sharply decrease to ∿1100 ppm ($CaCO_3$-free, salt-free) below 10 cm. This distribution supports remobilization of Mn from below 10 cm in the core and an accumulation in the oxic sediment above this region. Given a particulate flux of Mn to Station 24 sediment of 78 μg cm^{-2} y^{-1} (1300 μg/g x 0.06 g cm^{-2} y^{-1}) and a net accumulation rate of 66 μg Mn cm^{-2} y^{-1}, the net addition of Mn to the enriched zone in only 12 μg cm^{-2} y^{-1}. At this rate, it would take about 4200 y to accumulate the 50 mg of excess Mn found in the top 10 cm of this core. Even if the incoming particles had concentrations of 1800 μg/g, the accumulation period of the Mn-rich zone is still about 1200 years. In addition to Mn, Fig. 29 also shows evidence of Ni enrichment in the surface centimeters of sediment.

Lead and Cd concentrations ($CaCO_3$-free, salt-free) in Station 24 sediment are about 50% lower than the nearshore average and are equivalent to those found below the depth of anthropogenic input (20-50 cm) in sediments from Stations 11A, 14 and 15. It is interesting to note that the 0-2 cm sediment section from Station 24, which represents ∿25 years input, does not show a detectable anthropogenic contribution. This is probably due to bioturbation, since such mixing over a 10 cm length with a mixing coefficient of 10 cm^2/y (GUINASSO and SCHINK, 1975) and a sedimentation rate of ∿0.1 cm/y would effectively dilute surface input by a factor of 6, thus making it difficult to analytically discern.

Outer slope sediment from Station 4 (see location, Fig. 28) is characterized by a 40 cm deep surface carbonate layer. $CaCO_3$ concentrations of 25% in the surface 5 cm decrease to a relatively uniform 5% $CaCO_3$ below 40 cm (Fig. 30). Such layers in outer slope, rise and abyssal plain sediments usually delineate the increase in pelagic sedimentation associated with the Holocene epoch. Recent sedimentation rates, however, are reported to be on the order of 10-20 $cm/10^3$ y for this area (HOLMES, 1976 and references therein). Clay-size particles (<2 μm) made up 72% of the total Station 4 sediment ($CaCO_3$-free) with two thirds of the clay (47.8% of the total sediment) having <0.5 μm size particles.

Vertical metal profiles for Station 4 sediment (Fig. 30) are less uniform than those previously shown for nearshore and slope locations. Most of the elements have some marked subsurface maximum and are diluted in the more $CaCO_3$-rich surface sediment. Iron

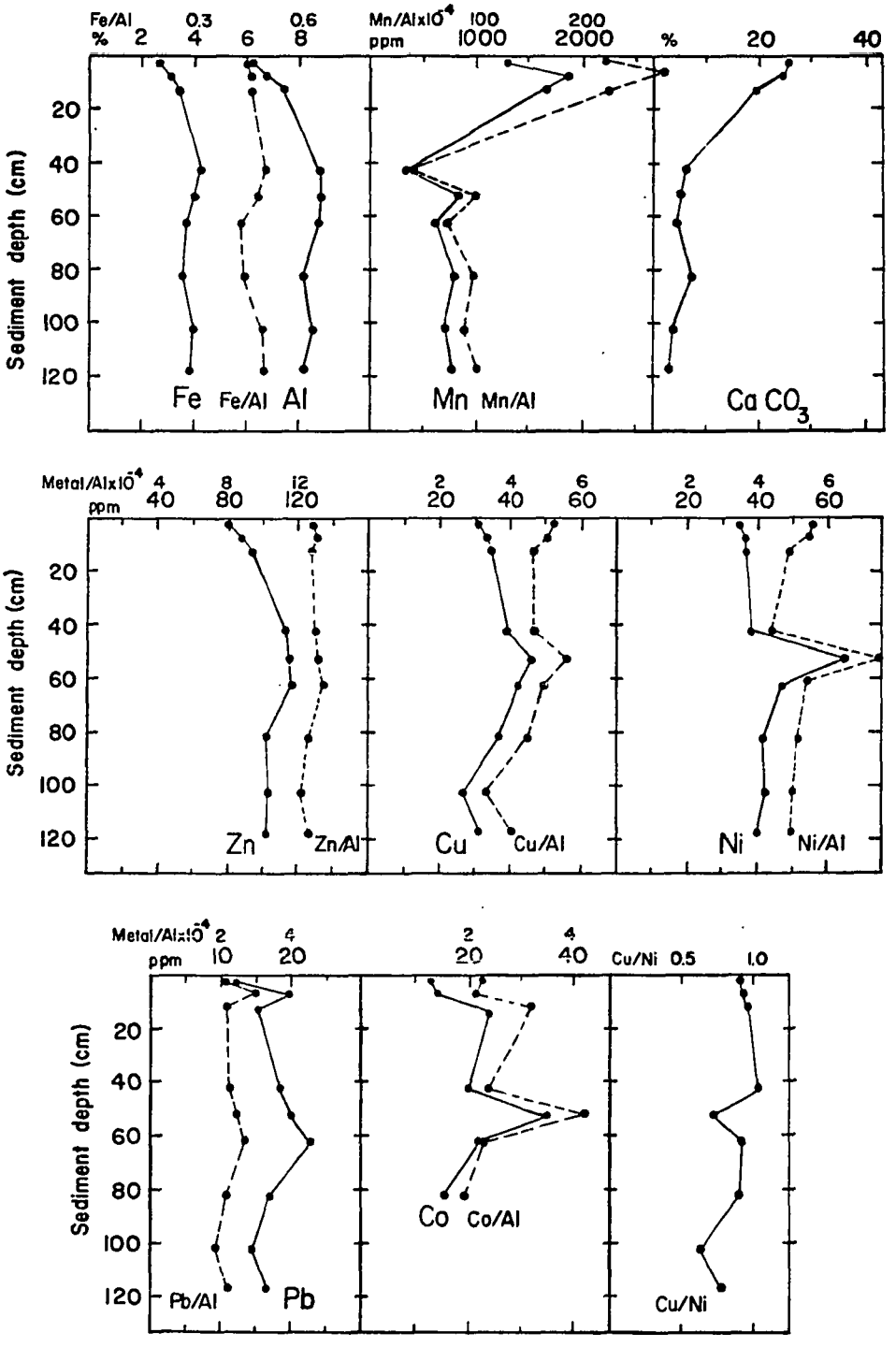


Fig. 30. Vertical metal and $CaCO_3$ profiles for Station 4 sediment (water depth 2710 m).

concentrations ($CaCO_3$-free, salt-free) are relatively uniform at 4.27 ± 0.32% with a maximum in the 40-45 cm section. These levels are comparable with those for nearshore sediment (4.22% Fe) yet lower than those for present-day Mississippi River suspended matter (4.61% Fe). The Al profile (Fig. 30) follows that for Fe closely and the Fe/Al ratio reaches a maximum at 40-45 cm and a minimum in the 60-85 cm section. No significant variations in the Fe/Al ratio (0.465 ± 0.026) are observed at Station 4. However there is a significant decrease in the Fe/Al ratio at Station 4 relative to river suspended material (0.533) and nearshore sediment (0.491). This decrease in the Fe/Al ratio will be discussed in the metal partitioning section.

Zinc behaves similarly to Fe (Fig. 30) and shows a mid-depth maximum and a very constant ratio to Al ($13.1 \pm 0.3 \times 10^{-4}$) and Fe ($28.3 \pm 1.7 \times 10^{-4}$). As in the case of Fe, Zn concentrations at Station 4 (120 ppm, salt-free, $CaCO_3$-free) and the Zn/Al ratio (13.1×10^{-4}) are lower than found in nearshore sediments (133 ppm and 15.5×10^{-4}).

Manganese concentrations are highest in the top 15 cm (1600 ppm) with a pronounced minimum (323 ppm) below this indicating a large scale remobilization of Mn via reduction-diffusion. Sediment from the 10-15 cm section were sieved at 62 μm and the coarse and fine fractions analyzed.

Fraction (μm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Ni (ppm)	$CaCO_3$ (%)
>62	1.71	1.75	3920	38	13.3	20.4	78
<62	4.09	8.55	1310	118	39.5	46.4	12
Total	3.39	7.40	1650	94	34.5	36.2	19

The data show that $CaCO_3$, which dominated the >62 μm fraction of the 10-15 cm section, provides a preferred surface for catalysis of Mn precipitation. This same preference for $CaCO_3$ by Mn was reported for another slope core by MCKEE (1977) who also showed scanning electron micrographs of Mn-coated $CaCO_3$ tests. Iron remobilization and precipitation on $CaCO_3$ tests is also suggested by the high Fe/Al ratio (0.977) in the coarse fraction and supported by the work of MCKEE (1977). In fact, the high ratios of Ni/Al (and to lesser degree Cu and Zn to Al) suggest that these metals have also been subject to post-deposition migration. The possibility that metal concentrations in the $CaCO_3$ fraction are high due to analytical error is small based on the background presented in APPENDIX B. The Pb/Al maximum for the total sediment in the Mn-rich zone may also be related to diagenetic processes.

Average Cu, Ni and Co concentrations for Station 4 sediment (42, 50 and 23 ppm respectively; $CaCO_3$-free, salt-free) are higher than those for nearshore sediments (Table 27, p. 137) but lower than or comparable to those for river particulates. These average values give no indication of any net metal enrichment due to physical sorting or chemical deposition. However, Cu, Ni and Co do show single point maxima in the 50-55 cm section (Fig. 30) where concentrations ($CaCO_3$-free, salt-free) are 53 ppm Cu, 74 ppm Ni and 40 ppm Co; all of which greatly exceed river particulate values. This enrichment is most likely a relict which resulted from remobilization of these metals during the end of the last glacial period when strong reducing conditions were induced by a higher

terrigenous sediment input (lower %$CaCO_3$) to the area. Enrichment of Mn in the surface sediments at Station 24 gives evidence of present-day Mn remobilization.

Lead and Cd concentrations at Station 4 (21 and 0.15 ppm; $CaCO_3$-free, salt-free) are rather constant over the length of the core at pre-pollution concentrations. Any possible surface sediment indications of pollution are obscured by the lower sedimentation rate and vertical mixing of the sediment.

Station 5 sediment from the continental rise - abyssal plain area (see location Fig. 28) is in many ways similar to that from Station 4 on the lower slope. There is a 50-60 cm layer with >10% $CaCO_3$. The top 15 cm are a calcareous ooze (>30% $CaCO_3$) with the lower section of the core (60-140 cm) having a uniform 7.6 ± 1.6% $CaCO_3$. The sedimentation rate for this core is on the order of 8-10 cm/10^3 y (HOLMES, 1976).

Particle size distribution in Station 5 sediment is skewed toward finer grained material with 80% clay ($CaCO_3$-free). Two-thirds of the clay (54% of the total sediment) is made up of <0.5 μm particles.

Vertical Mn distribution at Station 5 is characterized by three maxima (Fig. 31), the largest (4360 ppm) at 30-35 cm. A sharp minimum of 574 ppm is observed at the base of 30-35 maximum, again suggesting massive reduction/diffusion of Mn. Without interstitial water data, it is difficult to ascertain whether the 30-35 cm region is presently a region of active Mn remobilization. This section may be a relict and the top 20 cm, wherein there is a secondary Mn maxima, may be the active site of Mn precipitation.

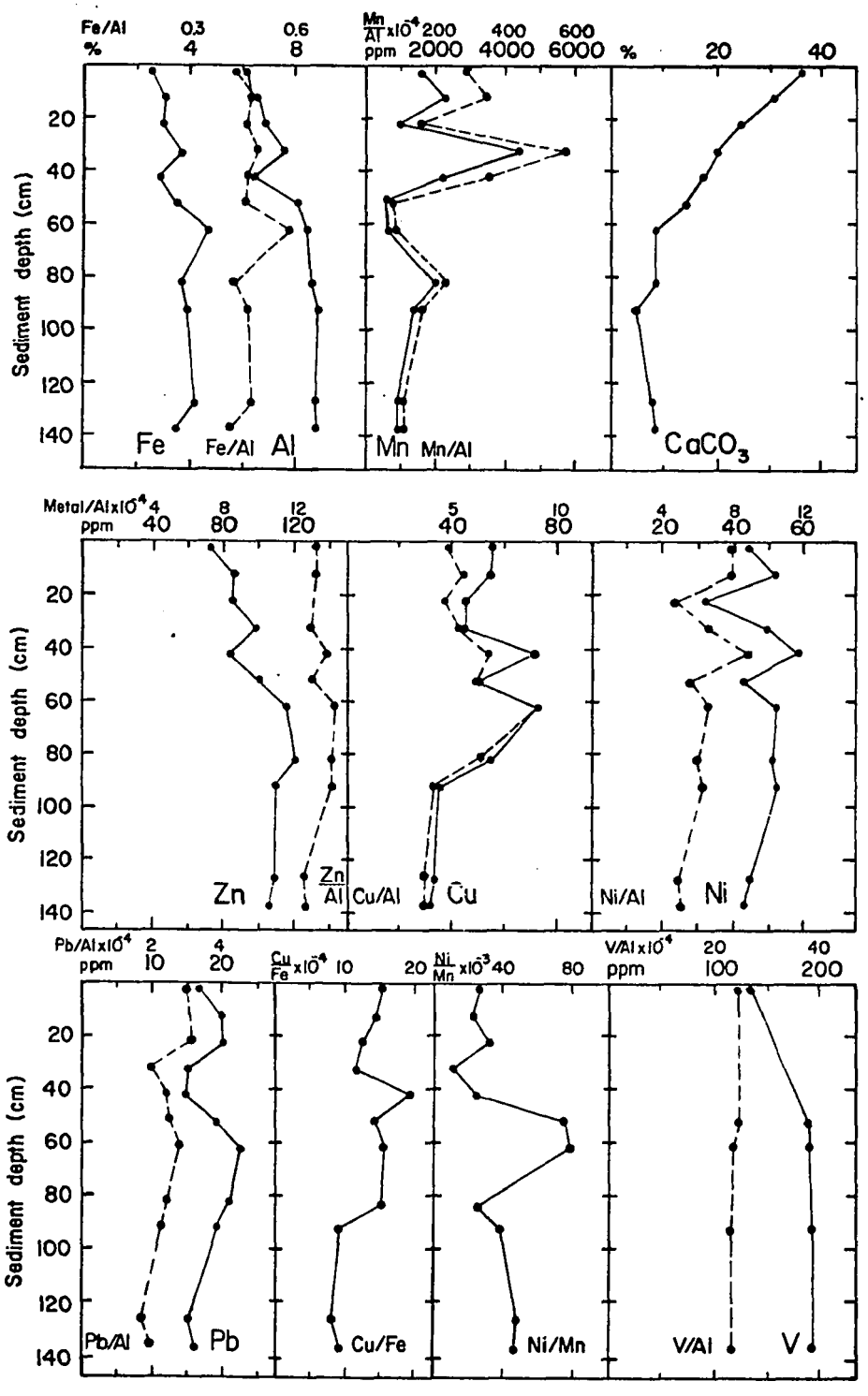


Fig. 31. Vertical metal and $CaCO_3$ profiles for Station 5 sediment (water depth 3350 m).

Iron concentrations are relatively uniform at 4.41 ± 0.50% ($CaCO_3$-free, salt-free), however minimum (3.56% at 40-45 cm) and maximum values (5.41% at 60-65 cm) are more pronounced than in slope or shelf sediments. Fe/Al ratios, excluding the Fe-rich zone, are also constant at 0.458 ± 0.023 and suggest a rather uniform mineralogy. A major deviation in the Fe/Al ratio occurs in the 60-65 cm section (0.583) and suggests either a gross mineralogical change or Fe remobilization. The latter explanation is supported to some degree by a lower Fe/Al value below the 60-65 cm zone and the behavior of Mn.

Zinc concentrations (125 ± 9 ppm, $CaCO_3$-free, salt-free) and the Zn/Al ratio (13.3 ± 0.6 x 10^{-4}) are constant in Station 5 sediment and suggest no enrichment of Zn from chemical deposition, physical sorting or diagenesis. Lead concentrations (23 ppm, $CaCO_3$-free, salt-free) show similar behavior to those for Zn. Vanadium values and the V/Al ratios for Station 5 are also remarkably uniform.

Copper and Ni profiles (Fig. 31) show considerable variation in the upper portion of the core, perhaps a result of post-depositional migration of these metals. Surface sediment Cu and Ni maxima (Cu, 64-84 ppm and Ni 68-79 ppm; $CaCO_3$-free, salt-free) are considerably above Mississippi River particulate values. However, in the deeper, low $CaCO_3$ portions of the core no maxima are observed and Cu, Ni, Mn and other metal values are closer to those for river suspended matter. This suggests that the more slowly accumulating surface (Holocene) sediment has slightly enriched (relative to Mississippi River

particulates) Cu, Ni and Mn concentrations. The trend may be somewhat complicated by diagenetic processes.

Sigsbee Knoll sediment from Station 6 (location, Fig. 28) may be categorized as a calcareous ooze with an average of 36% $CaCO_3$ (range 26-51%). Clay-size material (<2 μm) constitutes 80% of the $CaCO_3$-free sediment with 61% of the clay fraction (49% of the total sediment) having <0.5 μm particles. Sedimentation rates for this core are estimated at 3 cm/10^3 y (EWING et al., 1958; BURK et al., 1969) and thus the Holocene/Pleistocene boundary is within the top 40 cm. A zone of low $CaCO_3$ (26%) occurs at ∿40 cm (Fig. 32). This was also observed by EWING et al. (1958) and is related to an increase in detrital sedimentation at the end of the last glacial period.

Vertical metal profiles for Station 6 (Fig. 32) show Fe concentrations to be uniform with depth (4.65 ± 0.19% Fe; $CaCO_3$-free, salt-free), except for the 160-165 cm section which has only 3.44% Fe ($CaCO_3$-free, salt-free). The overall 4.65% value for the Sigsbee Knolls is the same as that for present Mississippi River suspended matter (4.61% Fe). Aluminum concentrations (9.88 ± 0.52% Al, $CaCO_3$-free, salt-free) are also constant with depth, yet 14% higher than those for Mississippi River suspended matter (8.65% Al). The Fe/Al ratio for Station 6 is very uniform (0.467 ± 0.016, excluding the low-Fe, 160-165 cm section where Fe/Al = 0.366). The ratio is similar to that found by TRASK (1953) for Gulf abyssal plain sediments (0.46), but lower than Mississippi River suspended matter (0.533) and nearshore Gulf sediment (0.493) values from this study

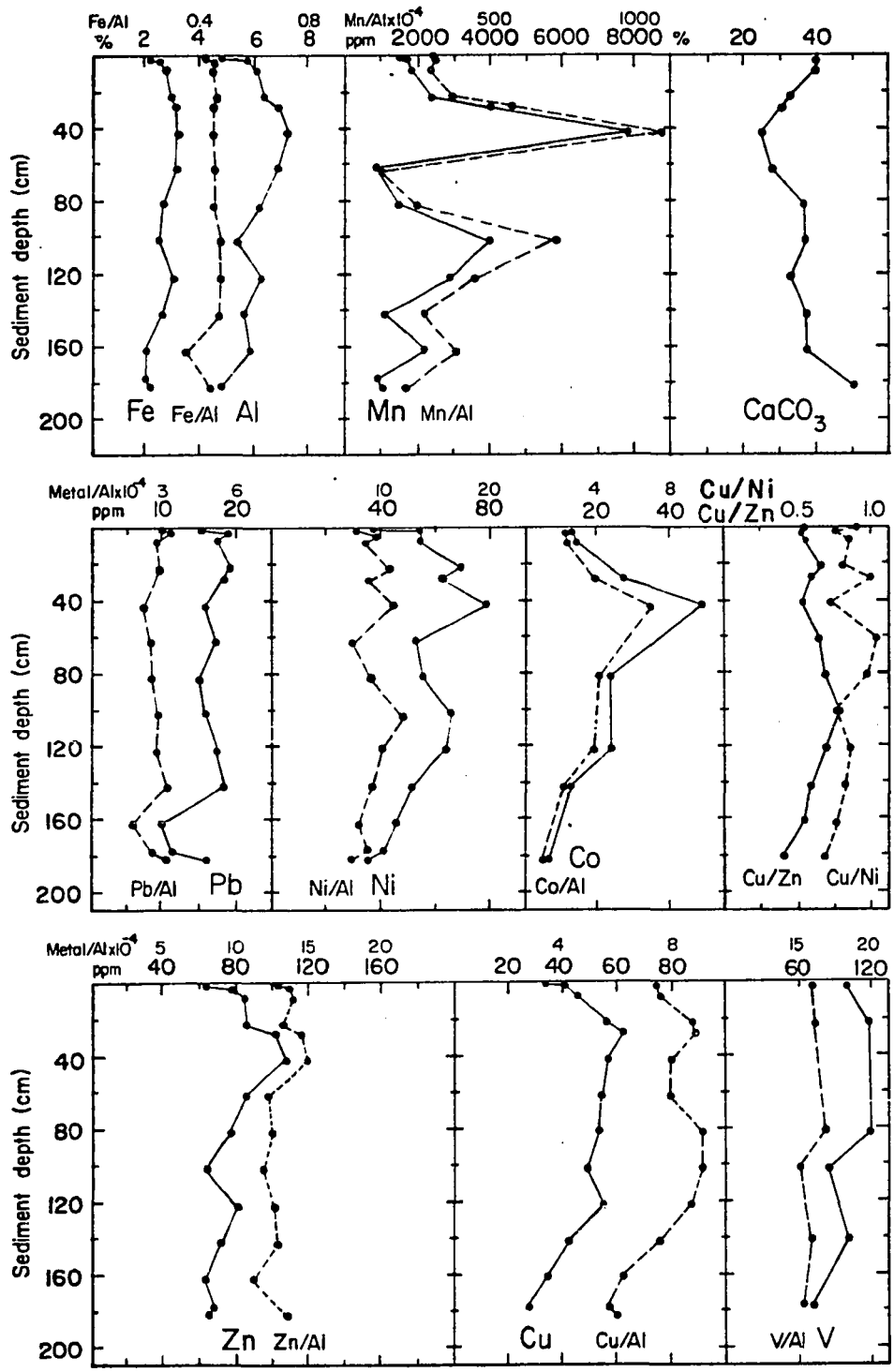


Fig. 32. Vertical metal and $CaCO_3$ profiles for Station 6 sediment (water depth 3400 m).

and Mississippi Fan values (0.526) from HOLMES and HEARN (1942).

The overall uniformity of Fe concentrations ($CaCO_3$-free, salt-free) in the Gulf of Mexico is consistent with observations made in the Atlantic, Indian and Pacific Oceans (EL WAKEEL and RILEY, 1961). Comparing present-day river particulates with sediments deposited hundreds or thousands of years ago in the deep Gulf of Mexico, however, may be hindered by changes in the composition of the source material over time. Furthermore, a small fraction of the lithogenous material in Mississippi province sediments has, even now, a source other than the Mississippi River. Despite the above difficulties, the constancy of Fe concentrations over time and distance from the source certainly suggests that scavenging of Fe by the deep Gulf particulates is small.

On the other hand, the decrease in the Fe/Al ratio from the river to the deep Gulf suggests either that physical sorting during transport has favored less Fe-rich clays or that there has been a recent change in river sediment composition. WHITEHOUSE et al. (1958) show that the settling rate of montmorillonite is much lower than that for illite and kaolinite. They also show that the Fe/Al ratio for Mississippi Delta and Gulf of Mexico montmorillonite is 2-3 times higher than that for illite and >10 times that for kaolinite. Clay mineral data for the Mississippi province (pp. 12-23) show that generally small changes in clay distribution occur. Surprisingly, reported montmorillonite percentages in knoll and abyssal sediments are somewhat lower than those for river particulates. However, a decrease in the river sediment load since the

early 1950's (Fig. 12, p. 77) may have biased the mineralogy of the particulates and thus the observed geographic distribution of clays. Diagenetic changes involving clays and Fe as well as the distribution of other minerals also complicate the observed decrease in Fe/Al from the river particulates to Gulf sediments.

Zinc and Pb concentrations at Station 6 are also vertically uniform (138 ± 12 and 28.4 ± 3.7 ppm respectively, $CaCO_3$-free, salt-free) except for the 160-165 cm section (Zn, 106 ppm; Pb 17.2 ppm). This marked covariance of Zn and Pb with Fe is consistent throughout the Mississippi distributive province. Furthermore, there is no change in Zn concentrations from nearshore to Sigsbee Knoll sediments and, as was the case for Fe, the Zn/Al ratio decreases away from the source. Comparison of river suspended matter and nearshore sediment Pb concentrations with those for the Sigsbee Knolls is constrained by the recent anthropogenic burden; however, Sigsbee Knoll Pb values (28 ppm, $CaCO_3$-free, salt-free) are about 25% higher than pre-pollution concentrations for nearshore sediments (22 ppm) suggesting some chemical deposition of Pb.

Vanadium concentrations correlate well with Al values and both show minima in the 100-105 cm section. The V/Al ratio for nearshore sediment (17.4×10^{-4}) is similar to that for the knolls (16.5×10^{-4}) suggesting no enrichment of V in deep Gulf sediment and strong covariance of these elements throughout the Mississippi province.

Manganese concentrations are very high in the 40-45 cm (11,000 ppm, $CaCO_3$-free, salt-free) and 100-105 cm sections (6670 ppm, $CaCO_3$-free, salt-free). These maxima correspond to ages of about 13,000

and 22,000 years B.P. and are probably related to climatological changes. BOSTRÖM (1970) observed similar, but lower concentration Mn maxima in Caribbean Sea sediment and related their occurrence to glacial periods. Possible explanations given by BOSTRÖM for the observed Mn peaks were (1) increased chemical weathering caused by pluvial conditions at lower latitudes which occurred at the same time that there were glaciers at higher latitudes, (2) more complete removal of Mn from seawater during cold periods, and (3) the formation of laterites on land during interglacial periods with subsequent removal to the sea during glacial stages.

A more probable mechanism for this Mn enrichment is that a sizeable flux of detrital sediment was deposited at the end of the glacial period and buried sufficient organic matter to bring about reducing conditions and remobilize Mn. The Mn-rich zone at 40-45 cm, Station 6, for example, is underlain by a sizeable minimum, indicative of Mn loss. Further support for Mn remobilization may be gained from analyses of the $CaCO_3$-rich coarse fractions at Station 6. The 5-10 cm section, as a whole, had a high but average Sigsbee Knoll total Mn concentration (1830 ppm Mn). In the coarse fraction (90% $CaCO_3$), the Mn concentration was only 334 ppm. However, in the Mn-rich 40-45 cm section (7800 ppm Mn) the $CaCO_3$-rich coarse fraction contained 18,000 ppm Mn and obvious Mn staining of the carbonate tests. This observation, which was also made in the slope environment (Station 24), can best be explained by large-scale remobilization of Mn in the sediment column. With the onset of the Holocene epoch and the decrease in sedimentation rate on the Sigsbee Knolls, the

Mn-rich zone was buried as a relict of its past environment. Copper, Ni and Zn concentrations are also at a maximum in the 40-45 cm section and may be related to the remobilization of Mn.

When referenced to Mississippi River particulates, Sigsbee Knoll sediments have higher concentrations of Co (+57%), Ni (+69%), Mn (+213%) and Cu (+73%). This marked difference is not found between river particulates and other deep Gulf sediments, even though both abyssal plain and knoll sediments have similar grain-size composition. One problem with this comparison is that 50% of the total sediment in both cases is made up of <0.5 μm particles. Thus the actual grain size distribution is not well known. The knolls have a 2-5 times lower sedimentation rate than the other deep Gulf sediments and this difference may be a more important determinant of metal enrichment.

Chemical partitioning data from sediment leaching experiments for Stations 24, 4, 5 and 6 are given in Table 29. This small (N = 14) data set well represents the overall deep Gulf population of this study (N = 45) and, with the exclusion of Fe-rich areas, seems fairly representative of central Gulf of Mexico sediments (HOLMES, 1976).

Iron is partitioned primarily between reducible and residual phases. Table 29 shows that residual Fe concentrations in deep Gulf sediments (2.47% Fe, $CaCO_3$-free, salt-free, which is 60% of the total Fe) are considerably higher than those found for Mississippi River suspended matter (1.96% Fe and 42% of the total). The residual-Fe/Al ratio is also increased (0.227 to 0.268), but by a smaller margin. This alteration in Fe partitioning is apparently due to

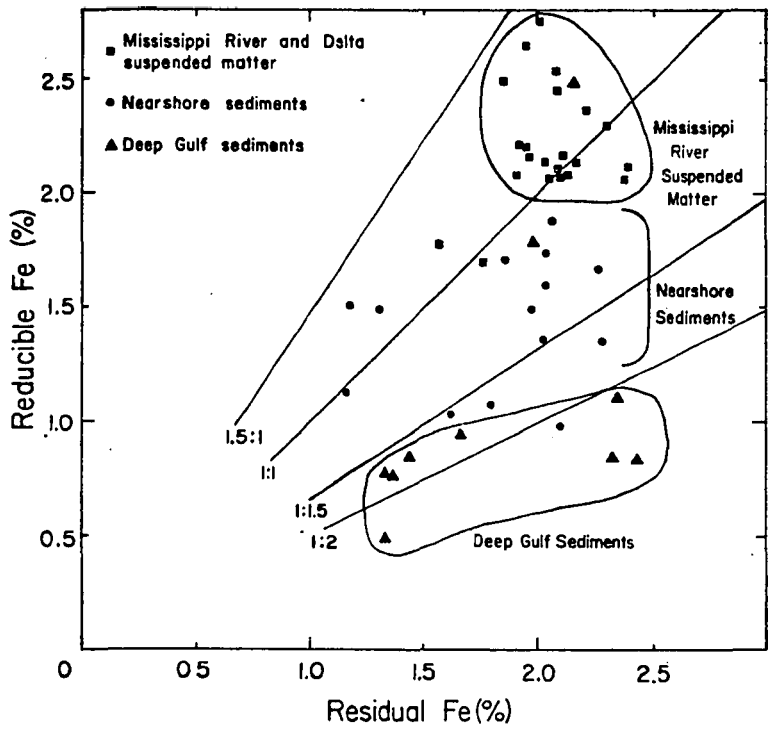
Table 29. Chemical partitioning of metals in Gulf of Mexico sediments

Station	Sediment depth (cm)	$CaCO_3$ (%)	Fe (%)					Mn (ppm)						Cu (ppm)					
			Red.	Ox.	Res.	Total (sum)	Total	Exch.	Red.	Ox.	Res.	Total (sum)	Total	Exch.	Red.	Ox.	Res.	Total (sum)	Total
24	0-1	-	1.03	0.30	1.62	2.95	3.22	103	4980	(112)	86	5280	5490	0.4	9.6	9.0	8.1	27.1	29.1
	0-5	16.2	1.07	0.26	1.80	3.13	3.33	107	12360	(235)	98	12800	13750	0.3	11.6	7.9	10.5	30.3	28.5
	60-65	13.1	1.49	0.25	1.98	3.72	3.93	119	769	30	104	1022	1060	0.5	13.9	4.6	5.9	24.8	24.9
	130-135	17.2	0.98	0.36	2.10	3.44	3.67	94	519	34	116	763	808	0.5	13.0	3.2	12.5	29.2	31.9
4	0-5	25.0	0.94	0.22	1.66	2.82	2.64	4	1161	29	96	1290	1294	0.9	9.9	7.5	14.2	32.5	30.5
	60-65	4.4	0.83	0.26	2.43	3.52	3.72	41	370	21	122	554	601	0.4	15.0	12.6	9.7	37.7	40.5
	115-120	3.0	1.10	0.24	2.34	3.68	3.84	38	526	30	123	717	762	0.5	6.1	8.1	13.2	27.9	30.9
5	0-5	36.0	0.76	0.15	1.36	2.27	2.53	19	1223	48	86	1376	1416	1.5	14.9	6.4	12.5	35.3	34.7
	60-65	8.6	1.79	0.45	1.98	4.22	4.69	42	479	37	118	676	684	4.4	19.8	22.2	9.2	55.6	-
	135-140	8.5	0.84	0.30	2.32	3.46	3.48	83	658	34	123	898	918	0.7	13.1	5.4	9.8	29.0	31.3
6	0-1	-	0.77	0.19	1.33	2.29	2.08	48	1460	39	86	1633	1513	1.2	10.4	14.8	8.7	35.1	34.5
	0-5	40.3	0.84	0.13	1.43	2.40	2.58	11	1565	56	86	1718	1773	1.8	13.3	7.2	17.6	39.9	41.2
	100-105	37.5	0.64	0.14	1.73	2.51	2.61	63	3880	(80)	-	-	3970	2.5	9.9	16.4	17.5	46.3	49.2
	175-180	50.8	0.49	0.14	1.33	1.96	2.01	-	-	-	-	-	-	1.4	8.1	7.6	12.6	29.7	27.4

(Note: all samples had <2 ppm Exch. Fe)

changes in the oxide phase and/or the silicate mineralogy. Fig. 33a shows that the reducible-Fe/residual-Fe ratio is about 1:1 or greater in the Mississippi River particulates and that it decreases to 1:2 with distance (and time) from the source. It seems unlikely that there is a net loss of the oxide phase and thus the decreased ratio is most likely due to the increased crystallinity of Fe minerals which makes them less susceptible to removal with dithionite. Part of this residual phase increase may also be related to the increased Al concentration of the deep Gulf samples (9.22 vs 8.65% Al) and the relatively constant residual-Fe/Al ratio throughout the study area (Fig. 33b).

Manganese is found predominantly within the oxide phase in deep Gulf sediments. For example, in surface sediments from Stations 24, 4 and 5 and in sediments from Station 6, up to 97% of the total Mn is present as an oxide, an increase from the 82% oxide-phase Mn in the river particulates. Subsurface sediment from Stations 24, 4 and 5 (low % $CaCO_3$, gray lutite), however, has only ∿70% of the Mn in the oxide phase which is more comparable with nearshore sediment values (∿69%). These relationships are presented graphically in Fig. 34a which shows that river and delta particulates have a reducible-Mn/residual-Mn ratio which scatters around 10 (excluding the low river stage, September 1975 samples). Manganese-depleted nearshore sediments and the subsurface gray lutite have ratios of <5:1. Finally, Mn-rich slope and deep Gulf sediments have ratios from 12 to 126:1, all of which re-emphasizes the extraordinary mobility of Mn.



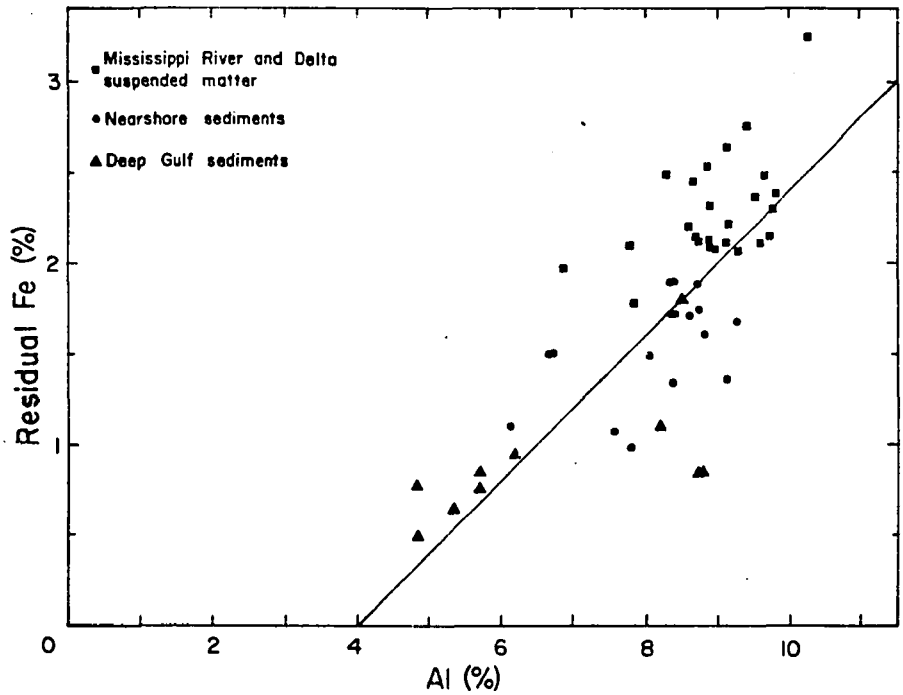


Fig. 33. a-b. (a) Reducible-Fe vs. residual-Fe and (b) residual-Fe vs. Al scatter plots for Mississippi River and Delta suspended matter and nearshore and deep Gulf sediments.

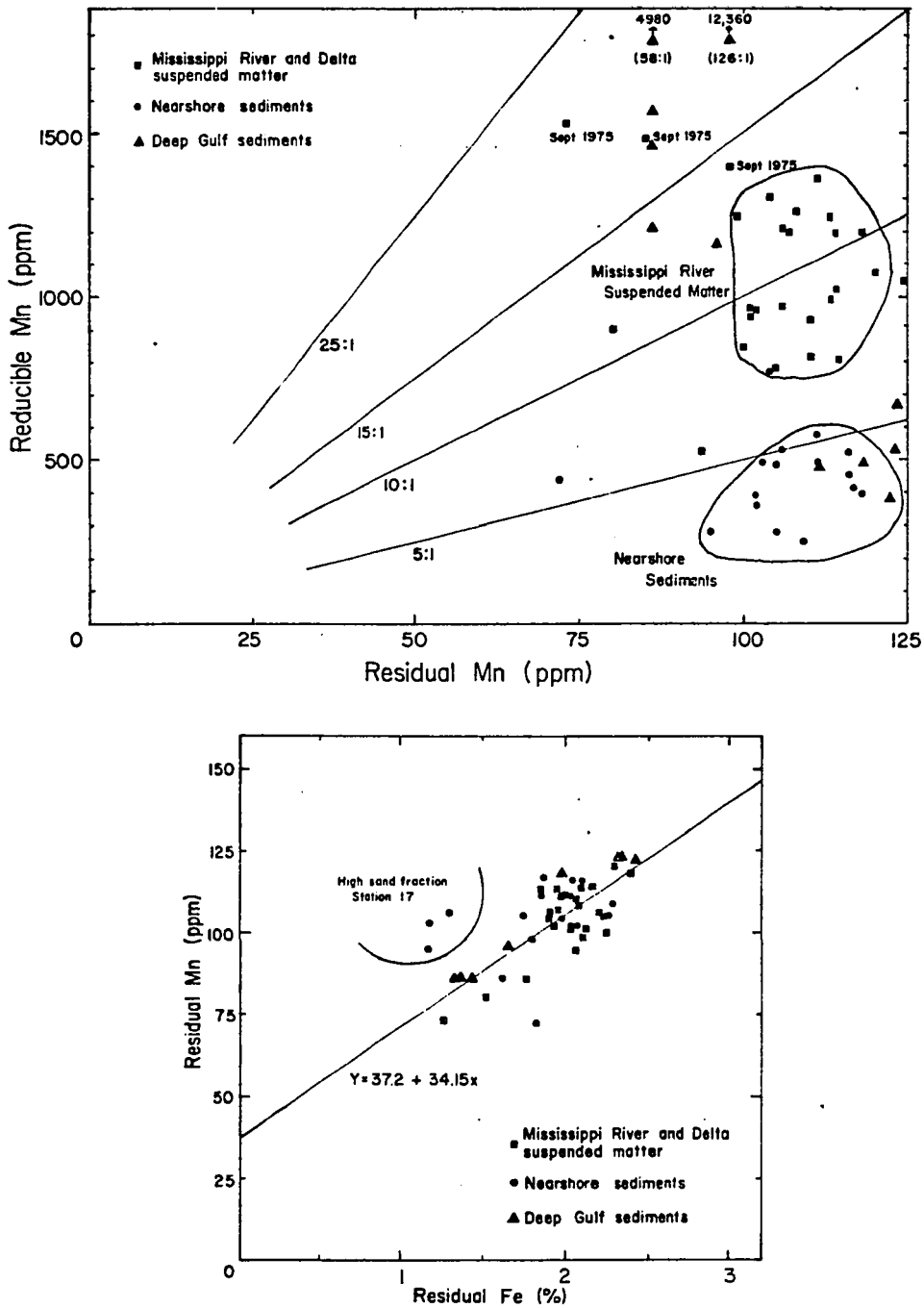


Fig. 34. a-b. (a) Reducible-Mn vs. residual-Mn and (b) residual-Mn vs. residual-Fe scatter plots for Mississppi River and Delta suspended matter and nearshore and deep Gulf sediments.

Residual Mn concentrations in deep Gulf sediments average 136 ± 11 ppm ($CaCO_3$-free, salt-free). The average is roughly 30% higher than that for river particulates (105 ± 13 ppm) and parallels the increase observed for residual Fe concentrations. Fig. 34b shows that the residual-Mn/residual-Fe ratio is constant over the entire study area excluding the silty-sand from Station 17.

The significant carbonate matrix in the deep Gulf samples may have hindered leaching studies for the other metals. For example, $CaSO_4$ precipitated in many samples during the dithionite treatment. Thus, the results for Cu, Ni, Pb and Co are not presented at this time.

SUMMARY AND CONCLUSIONS

This work has shown that even in a restricted area such as the Mississippi distributive province, significant physico-chemical changes involving some heavy metals can occur. These changes are primarily controlled by redox conditions and secondarily by mechanical and chemical deposition processes.

Suspended particulates transport >90% of the Mississippi River metal load. Chemical leaching of the river particulates showed that hydrous oxides and aluminosilicate lattices were the primary phases of metal transport. Iron and Ni were distributed evenly between oxide and lattice phases, Mn was present predominantly as an oxide coating, and Cu, Pb and Co had significant oxide, organic and lattice fractions.

In general, total and leachable metal concentrations in river suspended matter were seasonally and spatially uniform (i.e. variations <10% at 1σ). During low river flow, however, an increase in the organic content of particulates (from <3 to 25%) brought about a corresponding decrease in Fe and Al concentrations due to a dilution of aluminosilicate detritus. Particulate Mn, Zn and Cu concentrations were 30-40% higher and Cd values were 80% higher during low flow due to an association of these metals with the increased organic matter. Lattice concentrations of each metal, however, were lowered by $\sim$25% in the organic-rich suspended matter.

Average Fe, Cu, Cr, Co and Ni concentrations in Mississippi River particulates were $\sim$20% lower than average crustal abundance levels

whereas Mn values were about 40% higher. Suspended matter Pb, Cd and As concentrations were several times higher than crustal values due to an anthropogenic contribution of these metals. Average SiO_2, Al_2O_3, Fe_2O_3 and K_2O concentrations in Mississippi River particulates are similar to crustal abundances. Concentrations of Na_2O, CaO and MgO were 60-80% below crustal levels; however a high river dissolved load of these metals offsets the low particulate levels.

Mississippi River dissolved trace metal concentrations were at ppb and sub-ppb levels. This low dissolved load is probably controlled by adsorption of metal species on the abundant suspended matter (>300 mg/ℓ), a process known to be effective at the relatively high river pH (7.5 - 8.1).

No significant change in the total Fe, Al, Mn, Pb, Co, Cr, Ni or Cd concentration of river particulates was observed across the freshwater-seawater interface to the Gulf of Mexico. Such uniform metal distribution across the river-ocean boundary supports the conclusion that no significant desorption of any of the above elements occurs. For those elements which were chemically fractionated (Fe, Mn, Ni, Co and Pb) there also were no significant changes in partitioning across the river/delta interface. Particulate Cu and Zn concentrations, however, increased from the river to the delta. This increase may be related to an association of Cu and Zn with the increased percentage of organic matter in delta suspended material.

Mississippi Delta sediments had 20-50% lower Mn, Cu, Co, Ni and Zn concentrations and metal/Al ratios than river particulates. These changes occurred despite uniform Fe, Al, Cr and V concentrations and

similar grain-size distribution (especially in the 2-0.5 and <0.5 μm fractions) in river suspended matter and delta sediments. Chemical fractionation of the delta sediments showed that a reduction in oxide-phase metal concentrations accounted for the above depletions. Lattice-held Fe, Mn, Cu, Ni and Co concentrations in delta sediments were the same as those in river particulates.

Lead and Cd concentrations in surficial delta sediments were similar to those for river particulates yet 65 and 200% higher respectively than those for deeper (older) delta sediments. A time-dependent relationship for the excess Pb and Cd supports an anthropogenic source for these metals. The onset of this pollutant input is traced to the industrially active late 1800's. Lead inputs have increased at a greater rate since the late-1930's, a period of increased usage of Pb-additives in gasoline.

Reducing conditions in delta sediment promote a loss of oxide-phase Mn, Fe and perhaps other metals via reduction-diffusion. Interstitial water Mn gradients, in particular, support such a mechanism. Calculated fluxes of dissolved Mn from the surface centimeters of sediment to the overlying seawater range from 200 to >1000 μg Mn cm^{-2} y^{-1}. Losses of Mn by this mechanism are similar to those predicted from differences between the incoming flux of Mn and the flux of Mn buried at depth in the sediments. Iron fluxes from near-river-mouth sediments are also large (on the order of 1000 μg cm^{-2} y^{-1}), but bring about only a small percentage loss of the total Fe from the delta sediments. Measured losses of Cu, Ni, Co and Zn from delta sediments may also be related to a reduction-diffusion mechanism.

In nearshore Gulf areas where sedimentation rates are >0.5 g cm^{-2} y^{-1}, no Mn-rich surface sediment layer is found. The entire sediment column in these areas has lower Mn, Cu, Ni, Zn and Co concentrations relative to river particulates, even though Fe, Al and grain-size distribution are unchanged between the two environments. These observations, coupled with the interstitial water data, suggest that reduction-diffusion of metals is taking place in the surface millimeters of sediment.

The magnitude of the Mn loss from nearshore sediments (over an area of $\sim$1000 km^2 wherein s > 0.5 g cm^{-2} y^{-1}) is estimated to be 3.6×10^{10} g Mn/y. This flux is about six times greater than the total dissolved Mn load of the Mississippi River system. Similar calculations for Cu and Ni show that the sediment loss would be about equal to the river dissolved load for each. The projected Fe loss is about 45 times greater than the river dissolved load.

In outer shelf areas where sediment accumulation rates are on the order of 0.2 - 0.5 g cm^{-2} y^{-1}, a Mn-rich zone is found in the surface centimeters of sediment. However, the total excess Mn in the surface sediments is generally small. Interstitial Mn data suggest that a considerable portion of the remobilized Mn is diffusing into the overlying water or that surface sediments are being slowly winnowed away. In areas of lower sedimentation rate (<0.1 g cm^{-2} y^{-1}), the mass of excess Mn in the surface sediments is large and accumulating over time. No significant flux of Mn from the sediments to the overlying seawater occurs in these areas.

Dissolved Mn which diffuses from delta sediment is probably

oxidized and adsorbed onto the surfaces of the river-derived particles. The active hydrodynamics of the shallow water delta (i.e. ∿60 m water depth) favors removal of these higher Mn-bearing particles to outer delta and slope areas. In some cases the process may be repeated and sediment Mn concentration may be increased in step-wise fashion out to the deeper Gulf environments.

Manganese, Cu, Co and Ni concentrations are higher in deep Gulf sediments relative to river particulates (Tables 30 and 31). Observed metal enrichment is most striking in the strictly pelagic Sigsbee Knoll sediment where Cu, Co and Ni concentrations (ratioed to Al) are ∿50% above river particulate levels and Mn concentrations are almost triple river values. Little change in average Fe, Zn, Pb, Cr, and V concentrations occurs between nearshore and abyssal environments (Tables 30 and 31). Accompanying the changes in metal concentrations from nearshore to abyssal sediments is an increase in percent clay from 50 to 80% and a decrease in sedimentation rates from 1 g cm^{-2} y^{-1} to <0.02 g cm^{-2} y^{-1}.

Sigsbee Knoll and abyssal Gulf sediments have similar particle-size distribution (Table 30) and corrected Fe, Cr, V, Zn and Pb concentrations (Tables 30 and 31). Knoll sediments, however, have 50% higher Cu, Ni and Co concentrations and 125% higher Mn concentrations than abyssal sediments. The major distinguishing characteristic between these sediments is the 3-5 times lower sedimentation rates found on the knolls and it is this difference which suggests that chemical deposition is the dominant mechanism for metal removal.

The relative importance of chemical deposition is also supported

Table 30. Comparison of metal and clay concentrations ($CaCO_3$-free, salt-free) of Mississippi River particulates with nearshore, deep Gulf of Mexico and Sigsbee Knoll sediments

	N	Al (%)	Fe (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	$CaCO_3$ (%)	% Clay* 2-0.5μm	<0.5μm	S $g\ cm^{-2}y^{-1}$
Miss. River susp. matter	43	8.65	4.61	1300	193	46	45	21	79	55	1.3	150	~0.5	29	29	-
Nearshore sediments	88	8.59	4.22	968**	133	36	29	16	88	43	0.8	150	1.1	23	36	~1
Deep GOM sediments	29	9.25	4.38	2230	124	22	47	20	80	57	0.2	210	14	25	50	0.02
Sigsbee Knoll sediments	14	9.87	4.56	4070	133	28	78	33	75	93	0.4	170	36	31	49	0.002
$\delta M^{\dagger}$(Nearshore) (%)		-8	-26	-31	-22	-36	-24	11	-22	-40	0	-	-21	+24	-	
$\delta M^{\dagger}$(Deep GOM) (%)		-5	72	-36	-52	44	-5	1	4	-85	40	-	-14	72	-	
$\delta M^{\dagger}$(Knolls) (%)		-1	213	-31	-39	73	57	-5	69	-69	13	-	7	69	-	

* Clay percentages determined for deep GOM and Sigsbee Knoll on $CaCO_3$-free samples.

** Includes Mn-rich layers at Stations 14, 11A, 16 and 15.

$$^{\dagger}\ \delta M = \left[\frac{\left(\text{metal concentrations}\right)_{CaCO_3\text{-free, salt-free}}}{(\text{metal concentration})} - 1\right] \times 100$$

Table 31. Comparison of metal/Al ratios of Mississippi River particulates with nearshore, deep Gulf of Mexico and Sigsbee Knoll sediments.

	N	Al* (%)	Fe/Al	(Metal/Al x 10^{-3}) Mn/Al	Zn/Al	Pb/Al	Cu/Al	Co/Al	Cr/Al	Ni/Al	Cd/Al	V/Al
Miss. River susp. matter	43	8.65	0.533	150	22.3	5.3	3.2	2.4	9.1	6.4	0.15	17.3
Nearshore sediments	88	8.11	0.492	92	15.4	4.2	3.4	1.8	10.4	5.0	0.10	17.4
Deep GOM sediments	29	7.50	0.468	220	13.4	2.4	5.1	2.2	8.6	6.2	0.02	22.7
Sigsbee Knoll sediments	14	5.93	0.457	413	13.2	2.7	7.9	3.6	7.6	9.2	0.05	16.5
		$\delta M^{\dagger}$ (Nearshore) (%)		-8	-40	-31	-21	-35	-25	14	-22	-33	1
		$\delta M^{\dagger}$ (Deep GOM) (%)		-12	47	-40	-55	-2	-8	-6	-3	-87	31
		$\delta M^{\dagger}$ (Knolls) (%)		-14	175	-41	-49	52	50	-16	44	-67	-5

* Uncorrected Al concentrations.

† $\delta M = \left[\frac{\text{metal/(Al)}_{\text{sediments}}}{\text{metal/(Al)}_{\text{susp. matter}}} - 1\right] \times 100$

by the uniform Pb, Fe, Zn, V and Cr concentrations in sediments throughout the Mississippi distributive province. This uniformity suggests that fractionation of particles by size (in the fine fractions) is not an important determinant of metal content for the above elements and that their chemical deposition rates (unlike those for Mn, Cu and Ni) are too slow to be observed in the Gulf of Mexico. Lead, for example, has an estimated chemical deposition rate of 5 μg Pb cm^{-2} 10^{-3} y^{-1} (CHOW and PATTERSON, 1962), too low to measurably increase Pb concentrations in Sigsbee Knoll sediments (where s = 2 g cm^{-2} 10^{-3} y^{-1}).

All three deep Gulf cores (Stations 24, 4 and 5) show evidence of large-scale Mn remobilization with Mn concentrations in some layers as high as 1.5%. Nickel, and to a lesser degree Fe, Cu and Co, also show evidence of post-depositional migration. $CaCO_3$ tests were shown to be a preferred site for precipitation of the remobilized metals.

Manganese maxima are also observed in the Sigsbee Knoll core and appear to be related to post-depositional migration of Mn. This could occur if a sizeable flux of detrital sediment to the area at the end of a glacial period buried sufficient organic matter to bring about reducing conditions. Such a mechanism is supported by observed Mn minima below Mn-rich zones and by the high Mn content (2%) associated with coatings on $CaCO_3$ tests. Cobalt, Ni and Zn also appear to follow Mn in this diagenetic remobilization.

The factor pattern for the total data set (Table 32) summarizes metal distribution controlling factors in the Mississippi distributive province of the Gulf of Mexico. Factor 1, with high loadings for Fe, Al, Zn, Pb and minor loadings for Cu, Co, Ni and clay reemphasizes the overall importance of the aluminosilicates to sediment metal distribution

Table 32. Factor analysis of Mississippi River and Delta suspended matter and nearshore and deep Gulf of Mexico sediments

	Factor 1	Factor 2	Factor 3	Factor 4
Fe	0.96			
Al	0.92			
Mn		0.43	0.17	0.85
Zn	0.89		0.30	
Pb	0.74		0.44	
Cu	0.51	0.64	0.39	
Co	0.61	0.54		
Ni	0.40	0.52	0.62	0.17
$CaCO_3$	-0.66	0.65	0.14	
Sand	-0.81		0.40	
Silt		-0.76	0.53	0.22
Clay	0.57	0.46	-0.66	
Eigenvalues	5.323	2.531	1.811	1.003
Relative % of total	44.4	21.1	15.1	8.4
Cumulative %	44.4	65.5	80.6	89.0

in the Gulf. Iron, Al, Zn and Pb concentrations are primarily controlled by aluminosilicates and show no evidence of significant chemical alteration or enrichment (natural) in the Gulf. Although too few data points for V and Cr were available for incorporation into the factor analysis, these metals also behave similarly. Factor 2 with loadings for Mn, Cu, Co and Ni described the metals which are enriched in the clay-$CaCO_3$ sediments of the abyssal Gulf. Factor 3 is associated with the very nearshore sediments where there is less clay and $CaCO_3$ and where pollution (Pb, Cd and perhaps Zn) and a greater predominance of heavy minerals with associated metals are found. Finally, Factor 4 separates the Mn-rich zones found on the outer shelf, slope, and abyssal plain which are related to post-depositional remobilization of Mn.

Comparison of Mississippi River suspended matter with Gulf of Mexico sediments shows that for many metals (Fe, V, Cr, Zn and Pb) there is virtually no change in concentration. This is probably because the metals are tightly held in oxide coatings and crystal lattices and because the removal of dissolved species from seawater is too slow to be observed in the Gulf of Mexico. Other metals (Mn, Cu, Ni and Co), however, may undergo dramatic alterations. In rapidly accumulating nearshore sediments, for example, the surface-most sediment layers are reducing and thus oxide phase metals may be dissolved and diffuse into the overlying seawater. Those metals lost from deltaic sediments (Mn, Ni, Cu and Co) may subsequently be deposited in deep Gulf of Mexico sediments where concentrations of these metals are high relative to nearshore and river sediments.

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APPENDIX A

Mass Balance Calculations

The attempted mass balance is subject to many complications, the major problem being reliable metal concentration data. However, the simple overview presented here does give a general indication of important metal sources and sinks.

1. Input fluxes

   a. River dissolved input based on water flow of

      3.2×10^{16} ℓ/y (LIVINSTONE, 1963)

      and average river water concentrations of TUREKIAN (1969) unless unavailable or otherwise noted.

Metal	Concentration (µg/ℓ) TUREKIAN (1969)	Mississippi River (U.S.G.S., 1975 (and this study)
Fe	-	20
Mn	7	10
Zn	10	10
Cu	7	2 (value used)
Ni	0.3	1.5
Pb	3	1 (value used)
Cr	1	0.5
Co	0.2	-
	1	-

   b. River particulate input based on suspended sediment discharge of

      1.83×10^{16} g/y (HOMEMAN, 1968)

      and continental crustal abundance data of TAYLOR (1964).

APPENDIX A (continued)

Metal	Concentration (µg/g) Continental crust (TAYLOR, 1964)	Miss. R. suspended matter (this study)	Average shale (TUREKIAN and WEDEPOHL, 1961)
Fe	56,300	46,000	47,200
Mn	950	1,300	850
Zn	70	180	95
Cu	55	45	45
Ni	75	55	68
Pb	12.5	45*	20
Cr	100	80	90
Co	25	20	19
V	135	150	130

* Includes significant anthropogenic contribution.

c. Glacial flux based on estimated input of 2×10^{15}g/y (GARRELS and MACKENZIE, 1971) and metal concentrations for Weddell Sea glacial marine sediments (ANGINO and ANDREWS, 1968) or continental crustal abundances (TAYLOR, 1964).

Metal	Concentration (µg/g) ANGINO and ANDREWS (1968)	Continental crust TAYLOR (1964)	Granite (TAYLOR, 1964)
Fe	21,000	56,300	27,000
Mn	644	950	400
Zn	-	70	40
Cu	70	55	10
Ni	46	75	0.5
Pb	-	12.5	20
Cr	104	100	4
Co	20	25	1
V	158	135	20

APPENDIX A (continued)

d. Marine erosion flux based on discharge of 2.5×10^{14}g/y (GARRELS and MACKENZIE, 1971) and average shale concentrations of TUREKIAN and WEDEPOHL (1961).

Metal	Avg. shale (µg/g)
Fe	47,200
Mn	850
Zn	95
Cu	45
Ni	68
Pb	20
Cr	90
Co	19
V	130

e. Atmospheric dust flux based on particulate transport of 6×10^{13}g/y (GARRELS and MACKENZIE, 1971) and continental crustal abundance data (TAYLOR, 1964). These calculated fluxes are compared with those which may be extrapolated from Bermuda atmospheric particulate data of DUCE et al. (1976). Although DUCE's data is generally 2-4 x higher than predicted, this is expected, according to the authors, because of sample location (they would expect much lower values in the remote, open ocean).

Metal Flux	Calculated from flux-crustal data g/y	Extrapolated from DUCE et al. (1976) g/y
Fe	0.03×10^{14}	0.10×10^{14}
Mn	0.006×10^{13}	0.021×10^{13}
Zn	0.004×10^{12}	0.008×10^{12}
Cu	0.003×10^{12}	0.008×10^{12}
Ni	0.004×10^{12}	0.016×10^{12}
Pb	0.008×10^{11}	0.022×10^{11}
Cr	0.006×10^{12}	0.022×10^{12}
Co	0.015×10^{11}	0.001×10^{11}
V	0.008×10^{12}	-

APPENDIX A (continued)

f. Submarine inputs

Quantification of submarine inputs are difficult; ELDERFIELD (1976) estimates that magmatic leaching, deuteric alteration and halmyrolysis together contribute 0.39 x 10^{13} g Mn/y to the oceans. This is a significant 16% of the total Mn input to the ocean. One would not expect this input to be as quantitatively important for Fe due to the high continental input of Fe, however it is possible that the submarine fluxes of Cu, Ni, Co and perhaps Zn could be a significant portion of the total input of these metals. These fluxes are not well quantified and not included in this work.

2. Removal fluxes

a. Nearshore sediment flux calculated below using the river particulate load (1.83 x 10^{16}g/y; HOLEMAN, 1968), the area of the deep ocean (3.07 x $10^{18}cm^2$; MENARD and SMITH, 1966) and the average deep-sea clay accumulation rate ($0.3 g cm^{-2} 10^{-3} y^{-1}$; BROECKER, 1974, p. 31).

Nearshore sediment flux = river input - deep ocean flux

= 1.83 x 10^{16}g/y - (3.07 x $10^{18}cm^2$ x $0.3 g cm^{-2} 10^{-3} y^{-1}$)

= 1.74 x 10^{16}g/y

Sediment metal concentrations are from WEDEPOHL (1960) and this study.

	Concentration (µg/g)	
Metal	WEDEPOHL (1960)	Miss. Delta (this study)
Fe	-	40,000
Mn	850	700
Zn	-	128
Cu	48	28
Ni	55	41
Pb	16	36*
Cr	100	84
Co	13	15
V	130	140

* Includes significant anthropogenic contribution

APPENDIX A (continued)

b. Deep-sea clay flux is calculated from the area of the deep ocean ($3.07 \times 10^{18} cm^2$) multiplied by the average clay accumulation rate ($0.3 g cm^{-2} 10^{-3} y^{-1}$) and equals 9.21×10^{14} g/y.

Metal concentrations are from TUREKIAN and WEDEPOHL (1961).

Metal	TUREKIAN and WEDEPOHL (1961)
Fe	65,000
Mn	6,700
Zn	165
Cu	250
Ni	225
Pb	80
Cr	90
Co	74
V	120

c. Deep-sea carbonate flux is calculated from the area of the deep ocean ($3.07 \times 10^{18} cm^2$), the average $CaCO_3$ accumulation rate of $0.8 g cm^{-2} 10^{-3} y^{-1}$ (BROECKER, 1974, p. 83) and metal data for foraminiferal tests (TUREKIAN, 1965).

Metal	Deep-sea carbonate concentrations (µg/g)
Fe	1,400
Mn	55
Zn	15
Cu	12
Ni	18
Pb	8
Cr	9
Co	5
V	10

APPENDIX A (continued)

d. Ferromanganese nodules have been estimated by MERO (1972) to be forming in the Pacific Ocean at a rate of 10 million tons/y (10^{13}g/y). TUREKIAN and CHAN (1971) note that nodules cover 25% of the ocean bottom (excluding the Atlantic) and that the total surface area of the nodules is comparable to the total surface area of the deep ocean (3.07×10^{18}cm^2). Using an upper limit accumulation rate of 0.5 mg/cm^2-10^3y (BENDER et al., 1970) the rate of formation of nodules would be 1.5×10^{12}g/y. For the purposes of this balance, a probable upper limit of 10^{13}g/y will be used with the world ocean Mn nodule metal averages of CRONAN (1976).

Metal	Concentration (μg/g)
Fe	156,080
Mn	161,740
Zn	710
Cu	2,561
Ni	4,888
Pb	867
Cr	14
Co	2,987
Cd	8
V	558

APPENDIX B

Method-of-additions analyses and standard rock determinations by atomic absorption spectrophotometry

Good accuracy and precision in trace metal analysis by atomic absorption spectrophotometry are frequently hindered by sample matrix problems. Molecular absorption by the major constituents in the sample may lead to erroneously high values for a given trace element. Sample matrices may also depress absorbance for a given element by promoting ionization or the formation of oxides and other compounds. This appendix shows one approach used to understand and minimize these problems in the sediment trace metal analyses of this study.

To estimate the contribution of molecular (background) absorption to the total sample absorbance, the analytical line for a given element and a nearby non-resonance line for that element were monitored simultaneously. BILLINGS (1965) showed that satisfactory corrections could be made for molecular absorption in the analysis of Mn, Co, Cu, Ni, Pb and Fe using non-resonance lines. This means that background absorbing species absorb at approximately the same levels on both the absorbing and non-absorbing lines.

To identify chemical interferences, the method-of-additions (standard additions) analysis is most frequently used. Samples are spiked with small volumes of appropriate concentration standards. Three separate and different concentration spikes are generally made. One may calculate the concentration in the original solution by linear extrapolation.

As part of this study, method-of-additions (MOA) analyses with

APPENDIX B (continued)

background correction were carried out for samples with variable matrices. The three sets of figures on the following pages present the results obtained for Cu, Co and Pb in samples of varying $CaCO_3$ content. The original solution contained 0.3-0.5 g of dissolved sediment in 25 ml of 1N HNO_3. In each case, the metal concentration (in ppm) is given from (1) direct analysis with no background correction (A), (2) direct analysis with background correction (A-B), (3) method-of-additions analysis without background correction (the higher number written along the baseline) and (4) method-of-additions analysis with background correction (the lower number written along the baseline).

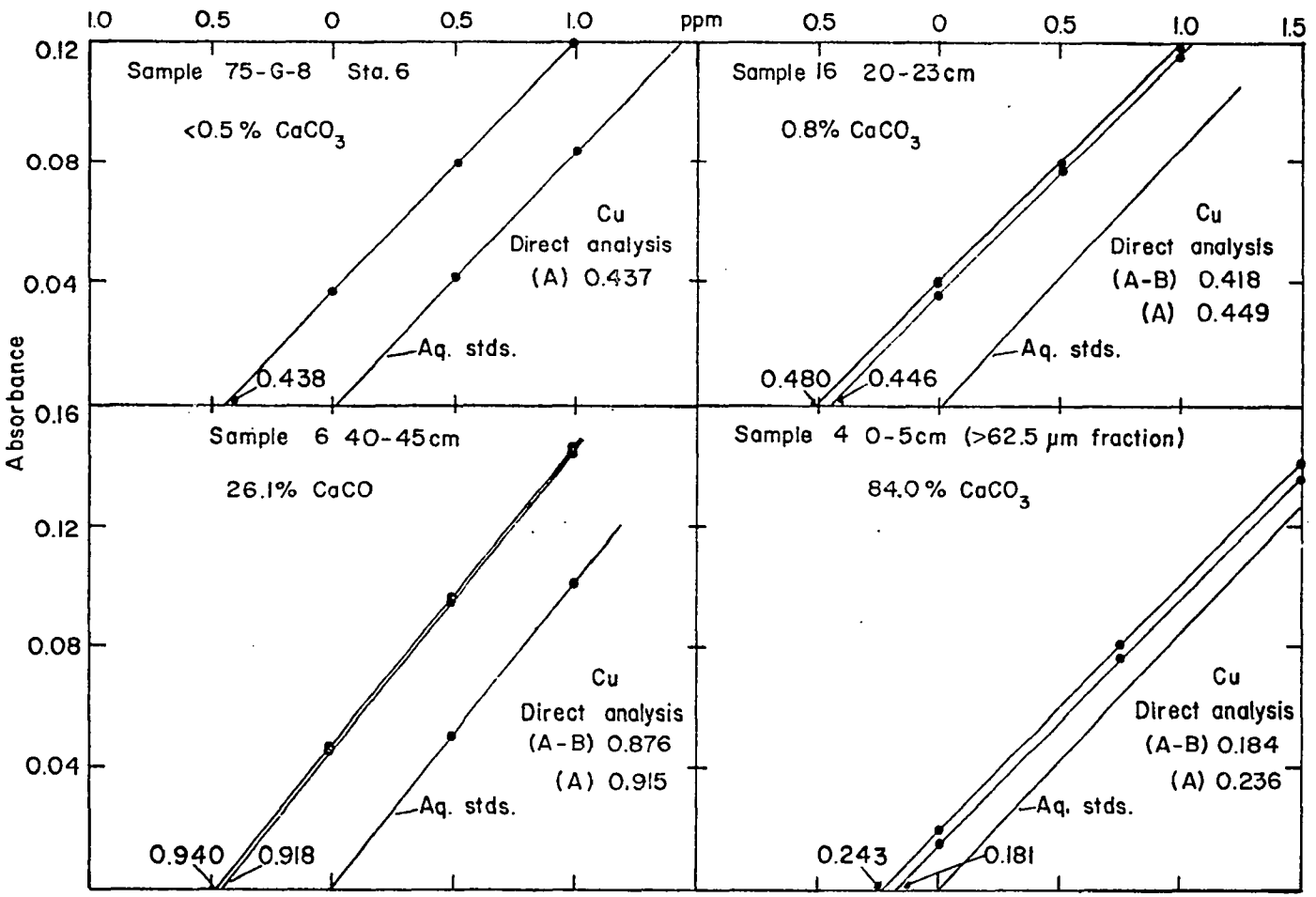
Standard curves for aqueous solutions containing each metal are also plotted. The good parallel relationship between aqueous standards and method-of-additions curves suggest no significant chemical interferences under the conditions of this work.

At low concentrations of $CaCO_3$, no molecular absorption for Cu is observed; however at 84 % $CaCO_3$, the background corrected value is 34% lower than the uncorrected value. In general, good agreement between direct analyses and MOA analyses was obtained.

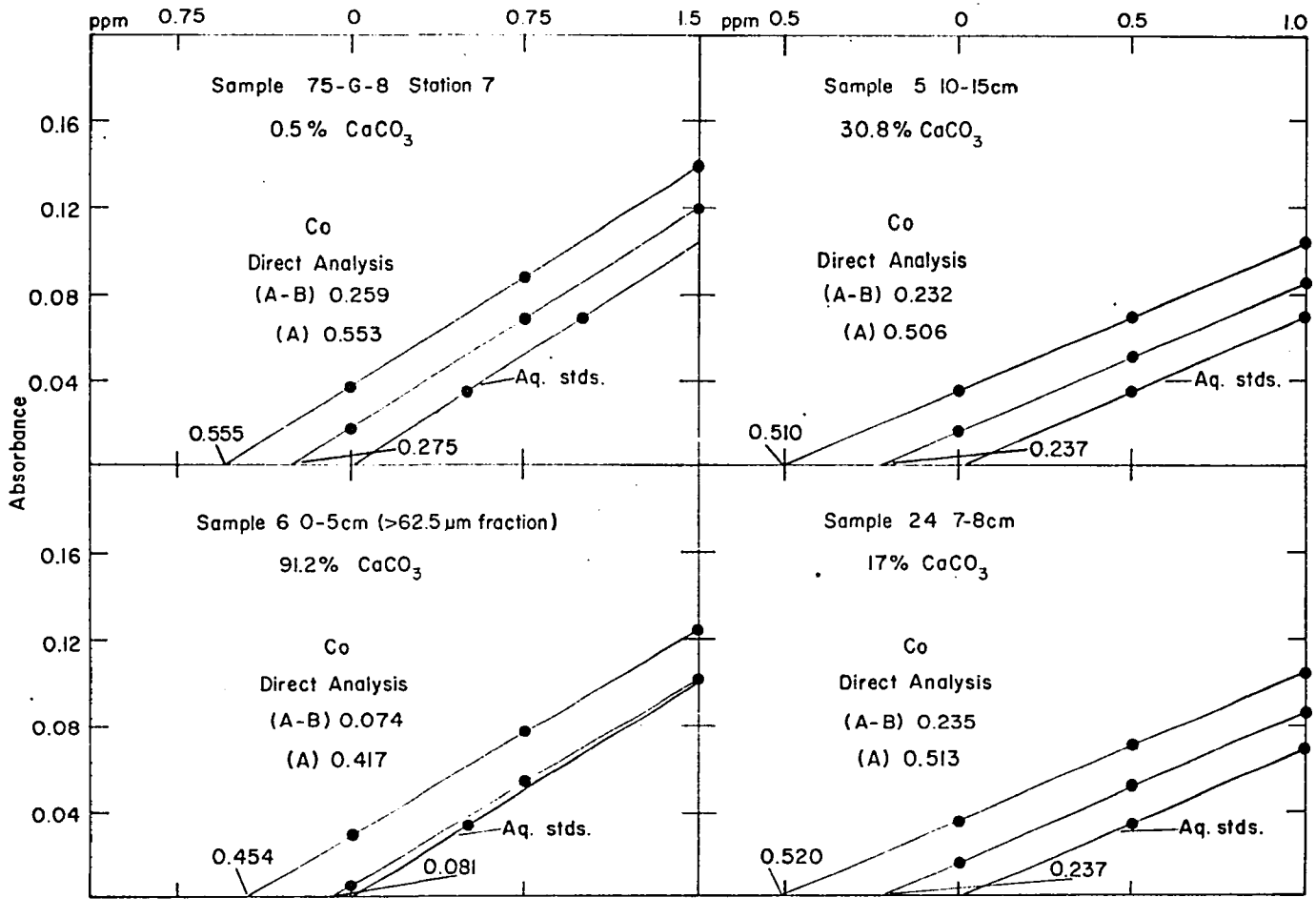
Similar procedures were carried out for the other elements studied. Molecular absorption for Co was significant even when $CaCO_3$ concentrations were negligible and is due to absorption by Fe in the solution. Similar behavior was also observed for Ni. Lead concentrations were distorted as a function of carbonate concentrations.

Comparison of direct analysis with MOA values were generally good throughout the study. Thus, most of my data was obtained by direct

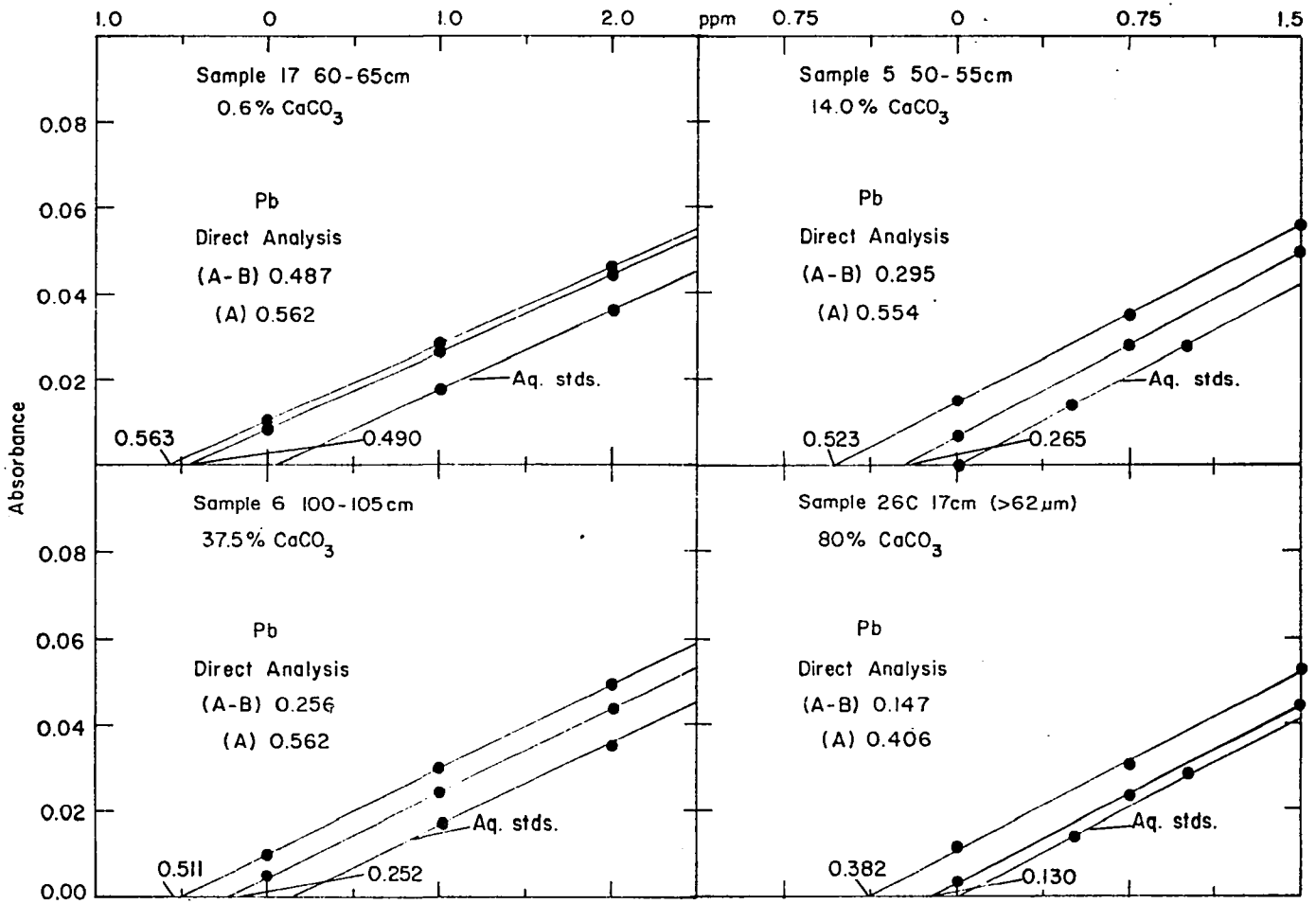
APPENDIX B (continued).



APPENDIX B (continued).



APPENDIX B (continued).



APPENDIX B (continued)

analysis with background correction. No correction for molecular absorption or chemical interference was required for Fe, Al, Mn or Zn analyses in this study.

The accuracy of the sediment metal values was checked by analysis of numerous U.S.G.S. standard rocks. Some of the results are tabulated below.

U.S.G.S. Rock		Fe (%)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Co (ppm)	Ni (ppm)
W-1	This study	7.76 (±0.03)	-	-	109 (±2)	9 (±2)	51 (±3)	71 (±5)
	FLANAGAN (1976)	7.78	1280	86	110	8	47	76
GSP-1	This study	2.93 (±0.13)	307 (±8)	105 (±1)	33.5 (±0.9)	55 (±2)	8 (±1)	12 (±1)
	FLANAGAN (1976)	2.95	331	98	33	51	6	12
G-2	This study	1.84 (±0.06)	248 (±11)	86 (±3)	11 (±0.5)	33 (±1)	10 (±1)	3 (-)
	FLANAGAN (1976)	1.82	260	85	11.7	31	6	5

FLETCHER (1970) presents results of analyses of U.S.G.S. standard rocks with and without background correction. The same approach was used in this study and both Fletcher's data and some data from this work are presented on the following page. These data show the importance of background correction to obtaining reliable data for some trace elements.

APPENDIX B (continued)

U.S.G.S. Sample	Investigator	I.D.*	Cu (ppm)	Pb (ppm)	Ni (ppm)	Co (ppm)
	This study	U	11.2	46.5	22.9	27.7
		C	11.2	33.3	3.0	10.4
G-2	FLETCHER (1970)	U	11.8	52.8	17.5	23.1
		C	11.4	20.6	8.1	10.4
	FLANAGAN (1976)	A	11.7	31.2	5.1	5.5
	This study	U	35.9	73.0	25.5	23.4
		C	33.0	53.0	12.3	7.6
GSP-1	FLETCHER (1970)	U	33.8	84.9	23.6	24.8
		C	31.6	50.5	10.1	9.2
	FLANAGAN (1976)	A	33.3	51.3	12.5	6.4

* U = uncorrected; C = corrected; A = U.S.G.S. value.

APPENDIX C

Mississippi River hydrological conditions for sampling periods during 1974-1975.

Hydrological conditions Cruise 74-G-9 29 May - 2 June 1974

Station	Depth (m)	Chlorinity (°/₀₀)	TSM (mg/ℓ)	POC (mg/ℓ)	Dissolved Silica (μM)	Temp. (°C)	Oxygen (ml/ℓ)	POC/TSM (%)
2 Venice	sfc	0.022	158	1.19	92	-	4.9	0.75
	8	0.022	259	1.69	91	-	4.6	0.65
	16	0.022	262	1.87	91	-	4.7	0.71
	sfc	0.020	143	-	89	23.8	5.0	-
	5	-	226	-	89	24.2	4.5	-
	8	-	258	-	90	23.0	4.7	-
3 Head of Passes	sfc	0.021	146	1.04	91	23.8	-	0.71
	4	-	231	1.45	91	23.8	4.6	0.63
	9	-	250	1.69	91	23.8	4.6	0.68
	sfc	0.021	158	1.22	87	24.1	3.9	0.77
	4	-	202	1.90	87	24.1	5.0	0.94
	9	0.021	332	1.82	89	24.0	4.7	-
	sfc	0.021	131	1.61	89	-	4.7	1.23
	3	-	226	1.49	89	-	4.7	0.66
	7	0.021	185	1.75	89	-	4.3	0.95
5 SW Pass	sfc	0.021	-	0.73	88	23.8	4.6	-
	2	-	-	1.07	89	-	5.0	-
	4	-	-	1.35	89	23.2	4.7	-
	6	-	-	-	89	24.1	4.7	-
	8	-	-	-	92	-	4.4	-
	10	0.020	-	1.64	89	-	4.7	-

APPENDIX C (continued)

Hydrological conditions Cruise 74-G-9 29 May - 2 June 1974

Station	Depth (m)	Chlorinity (°/₀₀)	TSM (mg/ℓ)	POC (mg/ℓ)	Dissolved Silica (μM)	Temp. (°C)	Oxygen (ml/ℓ)	POC/TSM (%)
6	sfc	0.022	232	1.33	92	24.4	4.6	0.57
So. Pass	3	0.022	281	1.39	93	24.2	4.7	0.49
	7	0.022	288	1.39	90	24.2	4.7	0.48
7	sfc	6.4	7.9	0.93	27	27.2	6.3	11.8
Outside plume,	3	8.2	5.7	0.51	24	25.6	2.0	8.9
Outside SW pass	4	14.5	-	-	22	25.5	2.3	-
	5	18.0	1.8	0.12	21	-	1.4	6.7
	7	18.7	2.4	0.08	16	-	5.8	3.3
8	sfc	3.4	75	0.56	78	24.1	4.5	0.75
In plume,	2	12.2	49	0.55	32	-	5.6	1.1
Outside SW Pass	4	16.5	4.9	-	6.0	24.8	6.4	-
	6	18.6	-	0.16	6.5	24.6	3.8	-
	12	19.4	9.4	0.15	7.2	-	3.0	1.6
	16	20.0	18.0	-	7.8	-	2.9	-
9	sfc	16.5	30.3	0.23	22	-	2.2	0.76
Outside	2	19.4	19.9	0.16	10.5	-	3.4	0.80
So. Pass	4	20.0	24.1	-	5.7	-	2.9	-
	6	20.0	16.3	0.17	5.5	-	2.8	1.06

APPENDIX C (continued)

Hydrological Conditions Cruise 75-G-1 26 February - 1 March 1975

Station	Depth (m)	Chlorinity (°/₀₀)	TSM (mg/l)	POC (mg/l)	DOC (mg/l)	Dissolved Silica (μM)	POC/TSM (%)
2	sfc	0.021	117	1.55	4.04	107	1.32
Venice	5	0.019	108	-	-	104	-
	10	0.018	160	1.51	3.18	101	0.94
	18	0.018	214	-	-	103	-
3	sfc	0.018	119	1.53	3.51	104	1.29
Head of	4	0.018	148	1.61	2.57	105	1.09
Passes	8	0.018	191	-	-	104	-
4	sfc	-	126	-	-	-	-
Pass à Loutre							
5	sfc	0.019	136	1.94	3.66	108	1.43
SW Pass	5	0.018	164	-	-	106	-
	10	0.018	161	1.65	3.87	104	1.02
6	sfc	0.020	172	1.46	3.46	106	0.85
So. Pass	4	0.022	174	-	-	105	-
	7	0.019	193	2.36	4.34	102	1.22
7	sfc	10.6	6.5	0.18	4.94	61.0	2.77
Outside	2	15.7	6.3	-	-	26.0	-
Plume,	8	18.9	7.5	-	-	14.6	-
Outside	12	18.4	12.4	0.15	2.90	14.9	1.21
SW Pass	20	19.3	1.6	-	-	2.5	-
	30	19.9	5.2	-	-	11.0	-
8	sfc	6.9	56.2	0.55	4.04	80.8	0.98
In plume,	2	9.8	52.2	-	-	65.2	-
Outside	5	17.7	22.8	-	-	18.0	-
SW Pass	12	18.8	17.6	-	-	7.8	-
	18	19.9	4.3	0.17	1.92	2.5	3.95
9	sfc	0.2	65.0	0.99	3.25	107	1.52
Outside	1	3.0	54.5	-	-	98.4	-
So. Pass	4	14.9	13.4	-	-	30.4	-
	9	19.5	4.8	0.14	3.05	3.2	2.92

APPENDIX C (continued)

Hydrological Conditions Cruise 75-G-8 10-14 July 1975

Station	Depth (m)	Chlorinity (°/₀₀)	TSM (mg/l)	pH	POC (mg/l)	DOC (mg/l)	Dissolved Silica (µM)	POC/TSM (%)
1	sfc	0.026	144	8.04	1.81	3.55	-	1.26
Buras	8	0.026	500	8.04	3.73	3.41	-	0.75
2	sfc	0.026	136	8.13	1.60	3.68	-	1.18
Venice	15	0.026	366	8.07	2.85	3.55	-	0.78
3	sfc	-	145	-	1.43	3.19	-	0.99
Head of	2	-	196	-	1.84	3.24	-	0.94
Passes	4	-	207	-	1.78	3.15	-	0.86
	6	0.027	254	-	1.73	3.15	-	0.68
	sfc	0.030	147	8.15	-	-	-	-
	2	0.030	215	8.13	-	-	-	-
	4	0.028	238	8.12	-	-	-	-
5	sfc	0.045	61	8.01	3.95	3.24	-	6.5
SW Pass	7	0.030	74	-	-	-	-	-
	14	5.92	203	-	1.18	3.13	-	0.58
7	sfc	7.7	31.8	8.39	0.37	2.29	76.0	1.16
Outside	2	10.6	21.9	8.40	0.34	2.18	45.6	1.55
Plume,	5	15.3	5.4	8.44	0.26	1.85	17.3	4.81
Outside	10	18.5	4.7	8.29	0.15	1.15	19.5	3.19
SW Pass	30	20.0	2.1	8.31	0.07	0.79	7.1	3.33
8	sfc	2.2	32.4	8.23	0.33	2.93	106	1.02
In plume,	2	17.7	12.4	8.52	0.17	1.39	13.8	1.37
Outside	4	19.1	14.0	8.47	0.17	1.03	13.7	1.21
SW Pass	6	19.5	21.3	8.48	0.19	0.98	13.7	0.89
	8	20.0	25.6	8.48	0.20	0.97	11.2	0.78
9	sfc	2.8	21.7	8.40	0.39	2.73	110	1.80
Outside	2	16.5	14.7	8.57	0.27	1.51	23.0	1.84
So. Pass	4	18.4	21.1	8.57	0.25	1.01	13.2	1.18
	6	19.5	19.4	8.56	0.22	1.05	8.0	1.13

APPENDIX C (continued)

Hydrological Conditions Cruise 75-G-11 7-9 September 1975

Station	Depth (m)	Chlorinity (°/₀₀)	TSM (mg/l)	pH	POC (mg/l)	DOC (mg/l)	Dissolved Silica (μM)	POC/TSM (%)
1	sfc	0.035	10.1	8.01	0.94	3.32	18.6	9.3
Triumph	2	0.034	10.9	8.03	-	-	18.5	-
	8	0.026	11.4	7.99	-	-	16.8	-
	12	0.029	13.6	8.00	1.05	3.21	16.8	7.7
3	sfc	0.25	10.7	8.00	0.82	3.36	19.8	7.7
Head of	3	0.23	9.9	-	-	-	19.8	-
Passes	6	0.24	11.7	7.99	0.88	3.00	21.0	7.5
4								
Pass à	sfc	-	9.8	-	-	-	-	-
Loutre								
5	sfc	0.42	8.4	8.01	0.76	2.50	13.2	8.6
SW Pass	2	0.67	8.8	8.01	-	-	14.4	-
	5	0.91	9.6	8.00	-	-	15.0	-
	12	10.8	30.5	8.15	0.88	1.98	14.7	2.9
6	sfc	0.70	8.9	7.99	1.15	-	18.6	12.9
So. Pass	1.5	0.60	8.9	7.97	-	-	23.4	-
	4.5	0.60	8.5	7.97	1.16	3.53	26.4	13.6
	6.5	2.47	16.9	7.97	-	-	26.2	-
8	sfc	11.2	5.2	8.51	0.83	3.20	8.1	16.0
Outside	1	11.2	5.5	8.49	-	-	6.8	-
SW Pass	2	11.3	5.5	8.42	-	-	6.7	-
	5	14.5	9.0	8.22	0.98	2.88	11.0	10.9
	10	17.9	12.8	8.10	-	-	8.1	-

APPENDIX C (continued)

Hydrological conditions Cruise 75-C-16 16-17 November 1975

Station	Depth (m)	Chlorinity (°/₀₀)	TSM (mg/ℓ)	POC (mg/ℓ)	Dissolved Silica (μM)	Temp. (°C)	DOC (mg/ℓ)	pH	$\frac{POC}{TSM}$ (x 10^2)
2	sfc		39.8	1.01	93	17.8	0.70	7.75	2.5
Venice	8		48.9	1.23	94	17.8	0.60	7.72	2.5
	12		60.4 ± 1.3	1.28	91	17.7	2.06	7.75	2.1
3	sfc		33.0 ± 3.0	0.97	94	17.8	3.94	7.77	2.9
Head of	4		40.1 ± 0.9	1.17	79	17.9	1.98	7.79	2.9
Passes	8		38.2	0.88	92	18.1	3.56	7.78	2.3
5	sfc*		28.7 ± 0.6	1.27	82	18.1	2.04	7.76	4.4
SW Pass	3	0.48	24.7	0.92	-	-	1.98	7.74	3.7
	6	1.52	25.0	1.04	-	18.2	3.21	7.78	4.2
	9*		19.5	1.20	73	-	2.99	7.92	6.2
	12	11.38	53.6	1.51	45	21.0	3.00	8.03	2.8
6	sfc*		37.8 ± 0.5	1.20	96	17.9	1.92	7.72	3.2
So. Pass	1.5		42.2	1.07	100	17.9	3.00	7.68	2.5
	4.5*		44.4	0.99	-	-	2.96	7.70	2.2
8	sfc	6.7	9.0	1.27	46	19.6	3.40	8.14	14.1
In plume,	2	8.6	8.1 ± 0.7	1.23	34	20.0	2.70	8.15	15.2
Outside	4	11.2	8.6	1.10	20	20.2	2.70	8.26	12.8
SW Pass	6	12.4	8.1	1.37	7	20.6	3.20	8.30	16.9
	10	18.0	6.6	1.19	9m 8	9m 22.6	-	8.20	18.0
					10	12m 24.4	2.40		
9	sfc	2.1	19.5	1.26	61.8	17.6	3.40	7.86	6.5
Outside	2	8.4	7.2	0.80	1m 63.0	1m 17.8	3.14	8.09	11.1
So. Pass	4	11.3	4.9	0.58	3m 21.0	3m 20.6	2.61	8.12	11.8
	6	15.3	3.8	-	5m 17.1	5m 21.8	-	8.14	-
	7	16.6	50.6	1.13	12.9	22.0	3.09	8.15	2.2
	8	16.8	-	1.66	-	-	3.66	-	-

* 30ℓ Niskin samples

APPENDIX D

Mississippi River and Delta suspended matter metal concentrations.

Cruise 74-G-9 29 May - 2 June 1974 River discharge* 16.4 x 10^6 ℓ/sec Suspended sediment discharge* 7.3 x 10^6g/sec

Station	water depth	Cl (°/₀₀)	TSM (mg/ℓ)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	POC/TSM (%)	Silt (%)	Clay (%)
2	sfc	0.022	158	4.96	-	1380	-	48.7	-	-	-	1.4	0.8	-	-
Venice	16m	0.022	262	4.92	8.75	1480	206	52.3	39.5	21.0	55.6	1.2	0.7	-	-
3	sfc	0.021	144	5.09	9.39	1420	205	50.2	41.1	20.8	60.8	1.2	0.7	-	-
Head of	sfc**	0.021	144	4.34	8.11	1350	179	44.4	43.8	17.2	60.3	-	-	49.8	50.0
Passes	4m	0.021	221	5.00	8.68	1320	206	53.6	44.9	23.9	62.0	-	0.6	-	-
	9m	0.021	256	4.90	9.12	1350	205	56.6	42.2	21.6	62.0	1.5	0.7	51.2 52.0	48.7 47.8
5	5m	-	-	4.94	8.76	1390	208	62.4	42.4	19.1	59.6	-	-	42.7	57.4
SW Pass	11m	0.020	-	5.06	9.11	1390	212	53.3	42.1	21.1	54.6	-	1.7	-	-
6	sfc**	0.022	232	4.39	8.58	1440	196	49.4	40.4	18.6	57.3	-	0.6	-	-
So. Pass	3m	0.022	281	4.92	-	1430	-	46.8	-	-	-	1.2	0.5	-	-
	7m	0.022	288	4.51	8.63	1460	189	41.0	38.6	-	57.5	-	0.5	-	-
8	sfc	3.4	75	4.82 (±0.13)	9.14 (±0.04)	1160 (±70)	206 -	82.7 (±5.5)	56.6 (±1.8)	22.0 (±1.3)	58.4 (±7.4)	1.6 -	0.8 -	20.3 -	79.6 -
In plume-outside SW Pass	sfc**	3.4	75	4.88	9.42	1610	240	48.9	45.5	19.2	63.6	-	-	-	-
9	sfc	16.5	30	4.53	7.81	1350	225	69.3	47.0	16.4	56.4	1.9	0.8	18.8	81.2
Outside	sfc**	16.5	30	4.67	9.08	1740	223	51.3	49.7	19.1	62.6	-	-	-	-
So. Pass	6m	20.0	16	4.81	7.88	1450	226	69.6	44.3	16.3	83.5	-	1.1	-	-
24 outside Pass à Loutre	sfc**	11.0	-	5.21	10.1	2440	-	45.2	48.5	20.8	56.4	-	-	-	-

* at Tarbert Landing, Mississippi (Data from U.S. ARMY CORPS OF ENGINEERS, 1976).

** Sample collected in 19ℓ plastic carboy.

APPENDIX D (continued)

Cruise 75-G-1 26 Feb. - 1 Mar. 1975 River discharge* 21.2 x 10^6 g/sec Suspended sediment discharge* 5.4 x 10^6 g/sec

Station	water depth	Cl (°/₀₀)	TSM (mg/ℓ)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	POC/TSM (%)
2	sfc	0.021	117	4.26	8.25	1110	154	36.3	35.6	19.9	54.0	1.3	1.3
Venice	7m	0.019	108†	4.37	8.10	1150	152	36.0	35.8	18.8	52.0	1.0	-
	14m	0.018	160†	4.82	8.77	1250	172	40.0	41.4	20.2	57.0	1.0	0.9
3	sfc-a	0.018	119	4.53 (±0.09)	8.30 (±0.15)	1160 (±6)	166 (±3)	40.3 (±2.5)	37.4 (±1.0)	18.8 (±0.6)	54.0 (±1.4)	1.1 (±0.1)	1.3
Head of Passes	sfc-b	0.018	-	4.40 (±0.11)	8.50 (±0.29)	1200 (±12)	166 (±8)	42.6 (±1.0)	38.7 (±0.9)	18.1 (±1.5)	55.5 (±1.1)	1.4 (±0.2)	1.1
	6m-a	0.018	148†	4.60	8.66	1250	179	42.8	40.0	18.8	57.4	1.0	-
	6m-b	0.018	-	4.28	8.66	1140	177	41.0	37.3	-	57.0	1.4	-
5	sfc	0.019	136	5.13	9.18	1200	202	47.3	46.2	19.6	62.7	1.5	1.4
SW Pass	8m	0.018	161†	5.02	9.02	1180	194	49.3	42.2	18.2	57.0	1.2	1.0
6	sfc	0.020	172	5.04	8.79	1256	166	46.6	44.9	22.6	58.6	1.3	0.8
So. Pass	6m	0.019	193†	4.76	8.66	1240	168	46.3	42.0	21.2	62.4	1.5	1.2
7	sfc	9	6.5	4.95	9.14	1020	230	94.0	62.8	19.9	63.4	1.4	2.8
Outside plume-outside SW Pass	12m	18	12.4	4.36	9.08	708	187	49.8	61.4	16.8	50.7	0.6	1.2
8	sfc	7	56.2	5.62	9.57	1000	233	70.1	74.1	19.5	62.6	0.9	1.0
In plume-outside SW Pass	18m	20	4.3	4.60	8.50	1190	192	52.6	85.5	20.2	59.3	1.8	4.0
9	sfc	0.25	65.0	5.83	10.25	1010	-	88.4	48.9	20.7	66.7	1.4	1.5
Outside So. Pass	5m	15	13.4	5.78	9.95	1090	242	90.6	67.2	21.8	65.5	2.0	2.9

* at Tarbert Landing, Mississippi (Data from U.S. ARMY CORPS OF ENGINEERS, 1976).

† TSM value from adjacent sample, see hydrographic data.

APPENDIX D (continued)

Cruise 75-G-8 10 - 14 July 1975 River discharge* 13.3 x 10^6l/sec Suspended sediment discharge* 4.4 x 10^6g/sec

Station	water depth	Cl (°/₀₀)	TSM† (mg/l)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	POC† / TSM (%)	Silt (%)	Clay (%)
1	sfc	0.026	144	4.66	9.05	1240	167	35.0	43.8	20.4	76	49.4	-	1.3	35.0	64.8
Buras	sfc**	0.026	144	4.56	9.37	1270	181	42.1	42.8	18.2	-	55.5	-	-	-	-
	8m	0.026	500	4.52	8.48	1350	159	39.8	40.9	22.1	-	51.9	-	0.8	-	-
2	sfc	0.026	136	4.52	8.74	1270	176	39.2	42.3	21.5	82	47.5	-	1.2	-	-
Venice	sfc**	0.026	136	4.76	9.32	1260	182	46.7	58.7	19.9	-	61.2	-	-	-	-
	15m	0.026	366	4.65	8.83	1410	164	41.3	44.6	24.1	-	49.2	-	0.8	-	-
3	sfc	0.030	145	4.55 (±0.18)	8.72 (±0.39)	1350 (±14)	180 (±5)	47.7 (±3.8)	48.1 (±1.6)	22.2 (±1.5)	80 (-)	52.0 (±1.3)	1.1	1.0	33.4 (±2.1)	66.4 (±2.1)
Head of Passes	4m	0.028	207	4.46	8.58	1370	172	49.2	49.1	24.8	-	51.3	1.3	0.9	31.8	68.1
5	sfc	0.045	61	4.83	9.10	1430	210	45.1	42.9	22.9	-	55.3	-	-	-	-
SW Pass	14m	5.9	203	4.49	8.89	1070	235	72.2	51.7	22.4	-	50.4	-	0.6	-	-
		salinity (°/₀₀)														
7	sfc	6- 8	32	5.01	9.69	1160	226	49.4	51.7	22.0	70	52.2	-	1.2	-	-
outside plume-	sfc	8-10	20-30	5.11	9.98	1130	249	51.3	49.6	-	103	60.5	-	-	-	-
outside SW Pass	sfc	14	20-30	5.01	9.33	1440	246	55.6	48.3	24.9	83	53.3	-	-	-	-
	sfc	16-18	20-30	5.09	9.74	1290	222	44.2	47.7	23.0	78	56.9	-	-	-	-
		30-35	2- 5	4.22	8.97	1840	303	-	55.4	-	-	57.8	-	3.3	-	-
8	sfc	5- 6	30	4.61	9.57	1050	234	43.7	46.6	21.8	73	52.1	-	1.0	29.1	70.6
In plume -	sfc	13-16	30	4.60	9.11	1030	214	43.8	53.2	-	97	54.5	-	-	-	-
outside SW Pass	4m	25-28	20-25	4.43	7.70	1190	210	43.9	42.0	21.7	83	48.8	-	-	-	-
	4m	33	20-25	4.36	7.78	1380	204	45.1	43.6	18.9	-	-	1.1	0.8	-	-
9	sfc	5, 12	20	4.13	8.87	1230	210	43.0	75.6	19.4	-	46.5	1.9	1.8	-	-
Outside So. Pass	sfc	12-13	20	4.98	9.51	1210	277	45.8	171	25.0	87	55.8	-	1.8	19.2	80.5

* at Tarbert Landing, Mississippi (Data from U.S. ARMY CORPS OF ENGINEERS, 1976).

** Sample collected in 19ℓ plastic carboy.

† See hydrographic data for further detail.

APPENDIX D (continued)

Cruise 75-G-11 7-9 September 1975 River discharge* 6.8 x 10^6 ℓ/sec Suspended sediment discharge * 0.9 x 10^6 g/sec

Station	water depth	Cl (°/₀₀)	TSM (mg/ℓ)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	POC/TSM (%)
1													
Triumph	sfc	0.035	10.1	3.56	6.24	1490	250	42.4	-	-	54.5	-	9.3
3	sfc	0.25	10.7	3.30 (±0.09)	6.69 (-)	1810 (±160)	262 (±13)	42.4 (±2.1)	61.6 (±1.1)	18.1	45.4 (±2.7)	2.1	7.7
Head of Passes	5m	0.24	11.7	3.58 (±0.26)	6.87 (±0.15)	1900 (± 34)	252 (±20)	45.5	61.6	18.9 (±1.6)	47.8 (±0.8)	2.4	7.5
5	sfc	0.42	8.4	2.83	6.11	1660	306	(75.8)	(167)	17.7	49.8	-	8.6
SW Pass	12m	10.8	30.5	4.45	8.69	788	184	48.0	46.3	-	49.4	-	2.9
6	sfc	0.70	8.9	-	-	-	-	-	-	-	-	-	-
So. Pass	6.5m	2.47	16.9	4.55	8.38	1340	204	49.6	50.2	-	50.5	1.6	-
8	sfc	7 - 10	5	3.71	7.23	2460	-	58.3	96	28.6	58.1	-	16.0
Outside	sfc	8 - 11	5	4.57	7.96	1860	-	55.5	59.0	23.3	49.7	-	-
SW Pass	5m	14 - 15	9	4.07	6.71	1600	-	50.4	51.3	20.9	50.4	-	10.9

* at Tarbert Landing, Mississippi (Data from U.S. ARMY CORPS OF ENGINEERS, 1976).

APPENDIX D (continued)

Cruise 75-G-16 16-17 November 1975 River discharge* 8.8 x 10^6 ℓ/sec

Suspended sediment discharge* 3.2 x 10^5 g/sec

Station	water depth	Cl (°/₀₀)	TSM (mg/ℓ)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	POC/TSM (%)
2	sfc	-	39.8	4.65	8.51	1210	207	-	53.6	30.7	60.2	0.8	2.5
Venice	12m	-	60.4	4.80	8.80	1290	190	43.9	45.0	22.5	54.6	-	2.1
3	sfc	-	33.0	4.79	9.16	1110	249	-	53.5	23.5	54.1	1.2	2.9
Head of Passes	8m	-	36.2	4.72	9.32	1140	197	51.9	46.8	28.3	54.3	1.4	2.3
5	sfc.	-	28.7	4.85	9.38	1120	256	52.3	63.1	24.1	-	-	4.4
SW Pass	8m	3.3	-	4.73	9.10	1210	208	45.1	58.6	31.0	56.4	2.0	-
6	sfc.	-	37.8	4.46	8.89	949	201	45.4	45.6	25.4	51.2	1.1	3.2
So. Pass	4m	-	44.4	4.57	9.34	1010	176	48.5	46.1	27.2	51.2	0.5	2.2
8													
In plume	sfc.	7-10	9.0	4.46	8.48	1270	299	53.9	64.5	22.1	51.5	1.2	14.1
Outside SW Pass	9m	14-17	6.6	3.70	7.45	1340	171	44.0	60.2	17.8	45.9	0.6	18.0
9	sfc	2.1	19.5	4.68	9.01	1240	328	74.4	64.0	28.4	68.7	0.8	6.5
Outside So. Pass	6m	15-16	3.8	4.28	8.37	1310	355	84.9	69.5	24.6	51.5	3.7	-

*at Tarbert Landing, Mississippi (Data from U.S. ARMY CORPS OF ENGINEERS, 1976).

APPENDIX E

Mississippi River Delta and open Gulf of Mexico sediment metal, $CaCO_3$ and grain size data.

Station 17 28° 52.85' N 89° 27.81' W Water depth 20 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-5	2.34	5.84	474	74	22.1	18.0	10.0	63	29.2	0.7	35.2	35.7	48.5	15.8
10-15	2.72	6.31	588	92	25.5	20.6	11.7	-	-	-	39.5	-	-	-
20-25	3.86	7.31	918	126	24.2	32.0	14.7	96	43.3	-	43.2	-	-	-
60-65	3.01	6.45	776	112	31.5	23.6	10.3	90	42.4	0.6	39.0	31.5	44.1	24.4
80-85	3.28	7.11	878	110	28.6	26.6	15.9	81	43.8	-	38.8	-	-	-
110-115	3.01	6.36	716	94	31.5	24.4	13.8	71	40.2	1.2	38.2	25.1	50.4	24.5
Mean (std. dev.)	3.04 (±0.51)	6.56 (±0.55)	725 (±170)	101 (±18)	27.2 (±3.9)	24.2 (±4.9)	12.7 (±2.4)	80 (±13)	39.8 (±6.1)	0.8 (±0.3)	39.0 (±2.6)	30.8 (±5.3)	47.7 (±3.2)	21.6 (±5.0)
Range	3.86 to 2.34	7.31 to 5.84	918 to 474	126 to 74	31.5 to 22.1	32.0 to 18.0	15.9 to 10.0	96 to 63	43.8 to 29.2	1.2 to 0.6	43.2 to 35.2	35.7 to 25.1	50.4 to 44.1	24.5 to 15.8

APPENDIX E (continued)

Station 8 28° 53.25' N 89° 31.80' W Water depth 30 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-2	4.23	7.98	668	138	39.4	31.1	15.8	-	45.9	0.8	-	-	0.2	55.6	-	-	-
2-4	4.29	8.05	640	-	41.7	29.6	-	86	40.7	1.1	127	8.12	-	54.8	0.5	35.3	64.2
4-6	4.15	-	619	-	37.4	30.0	14.3	70	39.8	1.1	-	-	-	54.7	-	-	-
6-8	4.12	7.86	657	128	38.5	31.2	14.9	87	40.4	1.1	-	-	-	56.6	-	-	-
8-10	4.10	7.90	771	129	36.9	31.1	-	68	38.2	-	110	7.79	-	53.0	0.3	40.6	59.1
14-16	4.12	7.82	681	-	38.3	30.6	-	77	40.0	1.1	-	-	-	53.5	-	-	-
15-18	4.15	7.95	746	142	-	34.7	14.2	-	36.0	-	-	-	0.2	56.6	-	-	-
18-20	4.20	-	700	-	40.3	32.1	-	77	42.0	-	-	-	-	54.9	-	-	-
20-23	4.10	8.23	608	146	44.3	31.3	-	-	47.4	-	131	8.29	-	53.2	0.2	40.7	59.1
28-30	3.73	7.60	621	-	41.9	29.1	17.6	79	38.6	1.4	-	-	-	51.7	-	-	-
41-44	3.56	-	600	113	36.0	28.0	-	77	-	-	-	-	0.2	51.2	-	-	-
44-46	3.60	7.66	610	126	36.9	29.5	17.6	-	37.3	0.8	113	7.51	-	47.3	6.7	43.0	50.3
58-60	3.58	7.25	621	-	32.0	29.1	15.9	-	40.0	0.9	-	-	-	42.4	-	-	-
Mean (std. dev.)	3.99 (±0.27)	7.83 (±0.27)	657 (±55)	132 (±11)	38.6 (±3.2)	30.6 (±1.7)	15.8 (±1.4)	78 (±7)	40.5 (±3.3)	1.0 (±0.2)	120 (±10)	7.93 (±0.35)	0.2 -	52.7 (±4.0)	1.9 -	39.9 (±3.3)	58.2 (±5.8)
Range	4.29 to 3.56	8.23 to 7.25	771 to 600	146 to 113	44.3 to 32.0	34.7 to 28.0	17.6 to 14.2	87 to 68	47.4 to 36.0	1.4 to 0.8	131 to 110	8.29 to 7.51	-	56.6 to 42.4	6.7 to 0.2	43.0 to 35.3	64.2 to 50.3

APPENDIX E (continued)

Station 10 28° 59.3' N 89° 04.7' W Water depth 50 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-2	4.23	8.05	713	142	55.5	33.1	15.4	90	40.8	1.3	0.4	51.2	0.6	42.2	57.2
2-4	4.06	-	690	-	39.4	31.2	-	-	38.1	1.3	-	46.5	-	-	-
4-6	4.16	-	720	143	37.6	31.6	18.1	98	40.0	0.9	-	46.9	-	-	-
6-8	3.86	7.90	701	132	38.7	31.8	17.6	87	42.7	1.2	-	48.7	-	-	-
8-10	4.18	8.17	742	145	41.0	31.7	-	74	42.2	1.0	-	53.0	0.1	34.0	65.9
14-16	3.94	7.55	839	125	37.6	31.6	17.5	68	38.4	1.2	-	50.1	-	-	-
15-18	3.95	7.52	864	129	40.3	33.2	14.4	-	-	-	0.5	50.9	-	-	-
18-20	4.25	8.33	853	-	45.5	32.7	-	102	42.4	1.6	-	51.2	0.1	37.4	62.5
28-30	4.37	8.27	808	143	42.2	33.2	15.2	70	45.7	1.5	0.6	53.1	-	-	-
44-46	4.11	8.26	704	155	43.4	32.8	19.5	67	43.0	1.3	-	57.5	0.1	42.1	57.9
52-54	4.34	8.07	829	-	46.8	32.1	-	95	44.3	1.3	0.5	56.2	-	-	-
Mean (std.dev.)	4.13 (±0.17)	8.01 (±0.30)	769 (±69)	139 (±10)	42.5 (±5.3)	32.3 (±0.7)	16.8 (±1.8)	83 (±14)	41.8 (±2.4)	1.3 (±0.2)	0.5 (±0.1)	51.4 (±3.5)	0.2 -	38.9 (±4.0)	60.9 (±4.1)
Range	4.37 to 3.86	8.33 to 7.52	864 to 690	155 to 125	55.5 to 37.6	33.2 to 31.2	19.5 to 15.2	102 to 67	45.7 to 38.1	1.6 to 0.9	0.6 to 0.4	57.5 to 46.5	0.6 to 0.1	42.2 to 34.0	65.9 to 57.2

APPENDIX E (continued)

Station 12 28° 57.0' N 89° 05.8' W Water depth 60 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-1	4.03	7.97	655	129	36.4	27.5	14.7	90	46.7	-	-	0.6	59.4	0.2	43.5	56.2
0-5	3.96	7.96	647	140	37.9	32.4	15.1	108	48.8	142	7.90	0.7	54.1	0.2	49.2	50.6
20-25	4.11 (±0.04)	8.07 (±0.14)	633 (±3)	144 (±3)	40.8 (±4.0)	30.2 (±0.5)	14.1 (±0.6)	105	46.3 (±1.7)	-	-	-	58.1	-	-	-
30-35	4.08	8.08	631	147	42.8	29.8	11.8	-	48.3	-	-	-	52.2	-	-	-
90-95	3.87	7.94	762	140	40.5	31.6	13.7	96	42.6	124	8.11	0.4	49.6	<0.1	46.5	53.5
110-115	4.29	8.85	600	134	41.6	34.5	15.9	-	42.6	-	-	0.4	52.8	-	-	-
120-125	4.12	8.35	606	136	37.3	32.6	14.3	98	45.8	-	-	-	51.7	-	-	-
140-145	3.52	7.42	707	116	29.3	25.0	16.6	72	45.9	-	-	-	48.9	-	-	-
160-165	3.91	8.00	652	127	31.1	29.2	15.0	67	42.1	125	7.75	0.7	49.5	7.6	44.0	48.5
Mean (std. dev.)	3.99 (±0.22)	8.07 (±0.38)	655 (±51)	135 (±10)	37.5 (±4.7)	30.3 (±2.9)	14.6 (±1.4)	91 (±16)	45.5 (±2.5)	130 (±10)	7.92 (±0.18)	0.6 (±0.2)	52.9 (±3.7)	-	45.8 (±2.6)	52.2 (±3.4)
Range	4.29 to 3.52	8.85 to 7.42	762 to 600	147 to 116	42.8 to 29.3	34.5 to 25.0	16.6 to 11.8	108 to 67	48.8 to 42.1	142 to 124	8.11 to 7.75	0.7 to 0.4	59.4 to 48.9	7.6 to <0.1	49.2 to 43.5	56.2 to 48.5

APPENDIX E (continued)

Station 16 — 28° 42.9' N — 89° 35.4' W — Water depth 110 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-2	4.29	8.28	1860	126	40.6	26.2	16.0	70	43.0	0.8	-	-	1.1	61.6	-	-	-
2-4	4.17	8.11	986	-	40.4	26.4	19.4	86	45.1	-	136	8.71	-	60.6	0.2	29.2	70.6
4-6	4.46	8.62	800	135	42.8	27.0	15.6	-	42.2	-	-	-	1.0	58.2	-	-	-
6-8	4.24	8.36	668	136	40.3	25.7	16.2	89	38.6	0.7	-	-	-	58.3	-	-	-
8-10	4.45	8.46	687	138	40.0	27.0	-	-	38.2	0.7	164	8.77	-	58.8	0.1	29.4	70.5
10-12	4.38	8.68	636	134	41.0	27.4	13.1	-	42.3	0.7	-	-	1.4	57.1	-	-	-
14-16	4.46	8.48	558	129	36.7	26.0	-	71	37.3	0.6	-	-	-	56.5	-	-	-
18-20	4.32	-	493	127	33.3	24.6	17.0	-	-	0.7	-	-	-	55.2	-	-	-
20-23	3.77	8.15	489	119	30.6	25.3	15.1	-	33.8	0.2	-	8.50	0.8	54.0	0.1	29.9	70.0
28-30	4.31	8.20	472	113	28.3	24.5	17.5	73	34.4	0.4	-	-	0.9	54.2	-	-	-
44-46	4.02 (±0.14)	8.20 (±0.10)	521 (±19)	112 (±3)	28.0 (±1.1)	25.8 (±1.5)	17.6 (±2.0)	87	36.9 (±3.0)	0.4	126	8.70	0.8	50.0	-	-	-
56-58	4.17	8.27	513	-	25.2	25.1	15.6	-	35.3	-	-	-	-	52.3	0.2	26.8	73.0
Mean (std. dev)	4.24 (±0.24)	8.35 (±0.19)	724 (±389)	127 (±9)	35.6 (±6.2)	25.9 (±0.9)	16.3 (±1.7)	-	38.6 (±3.5)	0.5 (±0.2)	142 (±20)	8.67 (±0.12)	1.0 (±0.2)	56.4 (±3.4)	0.2	28.8 (±1.4)	71.0 (±1.3)
Range	4.46 to 3.62	8.68 to 8.11	1860 to 472	138 to 112	42.8 to 25.2	27.4 to 24.5	19.4 to 13.1	-	43.1 to 33.8	0.8 to 0.2	164 to 126	8.77 to 8.50	1.4 to 0.8	61.6 to 50.0	-	29.4 to 26.8	73.0 to 70.0

APPENDIX E (continued)

Station 11 B 28° 53.5' N 89° 04.8' W Water depth 130 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-1	4.15	8.27	576	137	-	27.5	15.3	-	54.9	-	-	1.1	66.4	0.1	35.4	64.4
0-5	4.39	8.42	673	146	45.2	28.5	14.7	103	48.0	-	-	1.4	67.9	-	-	-
20-25	4.12	8.30	559	130	39.4	25.2	15.5	99	53.2	151	8.10	0.9	60.0	0.1	41.8	58.1
40-45	4.00	8.17	544	130	39.8	27.5	14.1	-	44.0	-	-	-	57.5	-	-	-
50-55	3.93	8.39	661	127	29.2	28.1	15.2	83	44.0	142	8.32	1.1	47.8	0.3	41.0	58.7
70-75	3.83	7.77	652	124	33.4	29.7	14.1	-	41.0	-	-	-	45.4	-	-	-
90-95	3.81	8.18	750	128	32.3	30.3	14.2	90	43.9	167	8.11	1.9	43.2	0.8	43.6	55.6
Mean (std. dev.)	4.03 (±0.20)	8.21 (±0.22)	631 (±74)	132 (±7)	36.6 (±5.9)	28.1 (±1.7)	14.7 (±0.6)	94 (±9)	47.0 (±5.3)	153 (±13)	8.18 (±0.12)	1.3 (±0.4)	55.5 (±10.0)	0.3 -	40.4 (±3.5)	59.2 (±3.7)
Range	4.39 to 3.81	8.42 to 7.77	750 to 576	146 to 124	45.2 to 29.2	30.3 to 25.2	15.5 to 14.1	103 to 83	54.9 to 41.0	167 to 142	8.32 to 8.10	1.9 to 0.9	67.9 to 43.2	0.8 to 0.1	43.6 to 35.4	64.4 to 55.6

APPENDIX E (continued)

Station 14 28° 38.3' N 90° 04.8' W Water depth 150 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-2	4.12	8.57	2260	122	35.3	23.1	15.0	41.4	-	156	8.40	1.7	59.8	-	-	-
2-4	3.84 (±0.03)	8.33 -	1800 (±20)	122 (±5)	31.0 (±1.5)	23.5 (±1.1)	14.9	35.9 (±1.6)	0.08	-	-	1.9	60.0	0.3	31.0	68.7
4-6	4.02	8.54	1760	119	33.3	23.8	14.6	35.7	-	-	-	2.5	59.0	-	-	-
8-10	3.80	8.36	1420	119	30.3	22.0	-	37.2	-	-	-	1.9	59.3	0.4	29.9	69.7
10-12	3.88	8.21	1410	113	27.6	22.6	13.4	41.0	0.05	163	8.63	-	58.8	-	-	-
13-16	3.87	8.34	1360	120	29.0	23.4	15.9	33.6	-	-	-	1.9	58.0	-	-	-
16-19	4.06	8.21	1210	122	26.4	21.8	18.2	32.2	-	141	8.59	2.0	57.7	0.1	29.5	70.4
25-28	3.92	8.36	1120	121	26.4	23.2	14.4	32.5	0.1	-	-	1.8	57.3	-	-	-
33-36	3.94	8.46	1060	120	25.8	22.6	-	39.2	0.3	-	-	-	55.8	-	-	-
40-42	4.00	8.13	1070	116	25.9	23.0	14.0	29.4	-	-	-	1.9	56.1	-	-	-
47-50	3.93	7.90	985	126	24.8	24.2	-	32.8	-	154	8.79	1.8	54.2	0.1	27.2	72.7
Mean (std. dev.)	3.94 (±0.10)	8.35 (±0.14)	1400 (±390)	120 (±3)	28.7 (±3.4)	23.0 (±0.7)	15.0 (±1.5)	35.6 (±3.9)	-	154 (±9)	8.60 (±0.16)	1.9 (±0.2)	57.8 (±1.3)	0.2 (±0.2)	29.4 (±1.6)	70.4 (±1.7)
Range	4.12 to 3.80	8.57 to 7.90	2260 to 985	126 to 113	35.6 to 24.8	24.2 to 21.8	18.2 to 13.4	41.0 to 29.2	-	163 to 141	8.79 to 8.40	2.5 to 1.7	60.0 to 54.2	0.4 to 0.1	31.0 to 27.2	72.7 to 68.7

APPENDIX E (continued)

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
Station 11 A		28° 48.9' N		88° 59.0' W			Water depth 480 m									
0-1	4.08	8.43	2630	124	38.8	25.9	15.3	-	40.6	-	-	3.4	67.0	.2	32.5	67.3
0-5	4.16	8.83	454	123	35.5	26.8	14.8	92	43.2	-	-	3.0	61.8	0.3	29.2	70.6
10-15	4.06	8.53	501	125	30.0	26.8	15.1	91	40.3	-	-	-	58.2	-	-	-
20-25	3.98	8.70	442	120	19.6	26.3	-	-	40.1	145	8.81	-	60.5	-	-	-
30-35	4.10	8.81	359	122	23.8	24.4	13.6	82	-	-	-	-	59.4	-	-	-
50-55	4.01	8.70	410	113	22.8	26.5	11.2	83	38.1	141	8.26	1.8	58.9	0.3	34.0	65.7
80-85	4.13	8.86	343	121	23.8	30.2	15.5	93	40.8	-	-	-	56.8	-	-	-
120-125	3.64	7.99	669	104	22.0	28.2	13.1	-	34.6	165 (±50)	8.34 (±0.13)	1.9	45.6	0.7	41.3	58.0
Mean (std. dev.)	4.02 (±0.16)	8.61 (±0.29)	726 -	119 (±7)	27.0 (±7.0)	26.9 (±1.7)	14.1 (±1.6)	88 (±5)	39.7 (±2.7)	150 (±13)	8.47 (±0.30)	2.5 (±0.8)	58.5 (±6.1)	0.4 (±0.2)	34.2 (±5.1)	65.4 (±5.3)
Range	4.16 to 3.64	8.86 to 7.99	2630 to 343	125 to 104	38.8 to 19.6	30.2 to 24.4	15.5 to 11.2	93 to 82	43.2 to 34.6	165 to 141	8.81 to 8.26	3.4 to 1.8	67.0 to 45.6	0.7 to 0.2	41.3 to 29.2	70.6 to 58.0
Station 10 A		27° 27.3' N		87° 35.6' W			Water depth 2680 m									
0-1	1.58	4.18	1070	54	11.3	22.1	9.0	32	32.8	-	-	45.2	-	-	-	-
Station 9		26° 26.5' N		86° 52.5' W			Water depth 2960 m									
0-1	2.67	5.85	1040	77	20.1	30.7	11.9	51	37.8	-	-	33.3	-	-	-	-

APPENDIX E (continued)

Station 15 28° 28.3' N 89° 41.0' W Water depth 510m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-2	4.40 (±0.02)	8.44 (±0.20)	7950 (±80)	128 (±2)	39.2 (±2.6)	27.4 (±0.7)	14.4	48.4 (±0.7)	-	1.9	67.0	-	-	-
2-4	4.23	8.42	1640	125	33.7	29.7	14.2	44.4	-	2.4	62.1	0.1	30.6	69.3
4-6	4.22	8.58	1130	125	29.8	27.4	14.8	39.1	0.4	-	61.8	-	-	-
6-8	4.46	8.80	1320	121	29.2	28.0	14.6	45.6	-	1.9	59.7	-	-	-
10-13	4.06	8.86	1020	123	24.4	26.8	18.2	39.1	0.2	1.6	60.9	0.2	22.6	77.2
15-18	4.08	8.51	1050	119	19.8	25.6	14.5	45.1	0.3	2.3	55.5	-	-	-
18-20	4.17	-	1300	116	20.2	25.9	14.6	38.8	-	-	56.3	0.1	23.5	76.4
25-28	3.67	8.25	642	111	23.4	24.2	14.0	36.0	0.2	1.8	56.2	-	-	-
33-36	3.26 (±0.13)	7.53 (±0.39)	710 (±40)	96 (±4)	18.8 (±1.2)	20.8 (±0.9)	14.1 (±1.6)	31.9 (±3.4)	-	-	49.6	-	-	-
38-41	4.19	8.90	662	118	22.5	26.3	14.8	36.9	-	1.3	53.1	-	-	-
44-46	3.68	-	960	121	23.8	27.9	14.5	33.9	-	1.8	54.2	0.1	29.4	70.5
Mean (std. dev.)	4.04 (±0.36)	8.48 (±0.42)	1670 (±210)	118 (±9)	25.9 (±6.4)	26.4 (±2.3)	14.8 (±1.2)	40.4 (±4.7)	0.3 (±0.1)	1.9 (±0.4)	57.9 (±4.9)	0.1	26.5 (±4.1)	73.4 (±4.0)
Range	4.46 to 3.26	8.90 to 7.53	7950 to 642	128 to 96	39.2 to 18.8	29.7 to 20.8	18.2 to 12.2	48.4 to 33.9	-	2.4 to 1.3	67.0 to 49.6	-	30.6 to 22.6	77.2 to 69.3

APPENDIX E (continued)

Station 24 27° 36.5' N 90° 09.0' W Water depth 1150 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-2	3.22	7.23	5490	105	17.7	29.1	-	-	54.5	0.2	-	-	-	62.6	-	-	-
0-5	3.33	7.26	13800	102	18.7	28.5	14.5	-	59.2	-	136	6.82	16.2	63.2	2.5	35.9	61.9
2-4	3.24	7.19	7660	100	16.4	27.9	-	-	(81.6)	0.3	-	-	-	62.4	-	-	-
7-8	3.30	7.30	10600	103	14.9	28.1	-	-	48.0	0.3	-	-	-	61.2	-	-	-
10-15	3.59	7.03	1020	101	16.1	28.5	12.0	62	46.0	-	-	-	18.7	60.1	-	-	-
30-35	3.46 (±0.06)	7.52 (±0.08)	946 (±12)	99 (±4)	17.2 (±1.3)	25.0 (±0.4)	14.7 (±1.0)	71 (±7)	51.2 (±1.3)	-	-	-	12.4	54.4	-	-	-
60-65	3.93	7.65	1060	103	17.4	24.9	15.1	-	41.3	-	167	7.68	13.1	53.9	3.1	29.7	67.2
105-110	3.53	7.47	887	108	16.1	28.7	16.1	69	46.5	-	-	-	12.8	55.9	-	-	-
130-135	3.67	7.39	808	109	17.1	31.9	14.0	86	56.0	-	152	6.97	17.2	57.2	2.7 (±0.1)	25.3 (±0.3)	72.1 (±0.2)
Mean (std. dev.)	3.47 (±0.23)	7.34 (±0.19)	- -	103 (±3)	16.8 (±1.1)	28.1 (±2.1)	14.4 (±1.4)	72 (±11)	50.3 (±6.0)	0.3 (±0.1)	152 (±16)	7.16 (±0.46)	15.1 (±2.7)	59.0 (±3.7)	2.8 (±0.3)	30.3 (±5.3)	67.0 (±5.3)
Range	3.93 to 3.22	7.65 to 7.03	13800 to 808	109 to 99	18.7 to 14.9	31.9 to 24.9	16.1 to 12.0	86 to 62	59.2 to 41.3	0.3 to 0.2	167 to 136	7.68 to 6.82	18.7 to 12.4	63.2 to 53.9	3.1 to 2.5	35.9 to 25.3	72.1 to 61.6

APPENDIX E (continued)

Station 4 26° 25.8' N 90° 31.7' W Water depth 2710 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-5	2.64	5.89	1290	79	12.1	30.5	13.0	34.1	0.10	136	6.66	25.0	50.0	-	-	-
5-10	3.07	6.71	1860	87	19.7	33.5	14.1	36.3	-	-	-	24.4	45.9	-	-	-
10-15	3.39	7.40	1650	94	15.4	34.5	23.5	36.2	-	-	-	19.4	43.8	10.2	31.0	58.8
40-45	4.18	8.34	323	113	18.3	39.1	-	38.0	0.13	-	-	6.2	57.3	-	-	-
50-55	4.00	8.42	820	115	20.2	46.8	34.9	64.6	-	-	-	5.1	67.3	-	-	-
60-65	3.72	8.71	601	117	22.9	42.7	19.2	46.8	-	167	8.65	4.4	55.5	0.3	29.5	70.2
80-85	3.56	8.14	775	102	16.9	36.5	15.1	41.2	-	-	-	7.1	58.9	-	-	-
100-105	3.96	8.08	692	103	14.6	26.3	-	42.0	0.13	-	-	3.8	74.6	-	-	-
115-120	3.84	7.75	762	102	16.6	30.9	-	39.8	-	240	7.90	3.0	61.2	0.1	25.7	74.2
Mean (std. dev.)	3.60 (±0.49)	7.72 (±0.91)	975 (±511)	101 (±13)	17.6 (±3.4)	35.6 (±6.4)	20.0 (±8.3)	42.1 (±9.2)	0.1 (-)	181 (±53)	7.74 (±1.01)	10.9 (±9.2)	57.2 (±9.9)			
Range	4.18 to 2.64	8.71 to 5.89	1860 to 323	117 to 79	22.9 to 14.6	46.8 to 26.3	34.9 to 12.9	64.6 to 34.1	-	240 to 136	8.65 to 6.66	25.0 to 3.0	74.6 to 43.8			

APPENDIX E (continued)

Station 5 25° 05.0' N 91° 29.0' W Water depth 3350 m

Sediment depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-5	2.53	5.51	1600	73	16.4	38.4	13.4	49	43.8	0.07	133	5.72	36.0	54.9	21.2	26.1	52.7
10-15	3.08	6.50	2260	86	19.8	44.1	13.4	-	51.7	-	-	-	30.8	50.6	-	-	-
20-25	2.99	6.48	1000	85	20.1	37.2	19.4	-	31.9	-	-	-	24.4	48.8	-	-	-
30-35	3.75	7.60	4360	98	15.0	42.6	20.4	-	49.6	-	-	-	20.0	50.8	-	-	-
40-45	2.82	6.10	2150	84	14.6	54.4	-	52	53.5	0.2	-	-	17.8	51.5	-	-	-
50-55	3.50	7.70	574	100	19.0	49.1	22.4	62	42.8	0.1	190	8.21	14.0	52.0	-	-	-
60-65	4.69	8.04	684	115	22.6	72.8	25.3	-	52.6	0.2	189	7.96	8.6	57.1	-	-	-
80-85	3.65	8.61	1960	121	21.0	54.7	26.1	54	51.0	-	-	-	8.5	60.2	0.7	15.5	83.8
90-95	3.88	8.38	1340	110	19.1	35.1	-	-	52.4	0.1	192	8.33	4.8	60.7	-	-	-
125-130	4.14	8.75	934	110	15.1	33.1	22.6	76	44.1	-	-	-	7.8	57.6	-	-	-
135-140	3.48	8.36	918	106	16.3	31.3	23.7	76	42.5	-	192	8.25	8.5	54.0	0.5	21.3	77.2
Mean (std. dev.)	3.50 (±0.62)	7.46 (±1.12)	1620 (±110)	99 (±15)	18.1 (±2.7)	44.8 (±12.3)	20.7 (±4.7)	62 (±12)	46.9 (±6.6)	0.1 (±0.09)	179 (±26)	7.69 (±1.11)	16.5 (±10.4)	54.4 (±4.1)			
Range	4.69 to 2.53	8.75 to 5.51	4360 to 574	121 to 73	22.6 to 14.6	72.8 to 31.3	26.1 to 13.4	76 to 49	53.5 to 31.9	0.2 to 0.07	192 to 133	8.33 to 5.72	36.0 to 4.8	60.7 to 48.8			

APPENDIX E (continued)

Station 6 23° 42.5' N 92° 29.6' W Water depth 3400 m

Sediment Depth (cm)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Cu (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cd (ppm)	V (ppm)	Al INAA (%)	$CaCO_3$ (%)	H_2O (%)	Sand (%)	Silt (%)	Clay (%)
0-1	2.08	4.83	1510	63	15.1	34.5	15.3	38	37.7	-	-	-	-	-	-	-	-
0-5	2.58	5.55	1770	78	18.9	41.4	13.0	-	53.8	0.4	99	5.89	40.3	51.1	-	-	-
5-10	2.79	6.05	1830	84	17.6	46.0	14.5	49	53.8	-	-	-	40.3	49.7	30.7	29.8	39.5
20-25	3.02	6.38	2400	85	19.3	56.2	-	-	69.2	-	118	6.49	33.5	50.3	-	-	-
25-30	3.19	6.92	4060	101	18.4	61.8	27.1	72	62.4	-	-	-	31.0	48.9	-	-	-
40-45	3.26	7.05	7800	107	16.1	56.7	49.0	34	78.5	0.2	-	-	26.0	47.7	-	-	-
60-65	3.20	6.82	890	85	17.5	54.4	-	55	52.2	0.2	-	-	28.8	46.3	-	-	-
80-85	2.71	5.81	1470	77	15.1	53.3	23.6	51	55.1	-	118	5.83	37.0	46.9	-	-	-
100-105	2.61	5.36	3970	64	15.7	49.2	-	38	65.0	-	82	5.19	37.5	46.2	-	-	-
120-125	3.08	6.27	2860	80	17.4	54.8	24.0	-	63.6	-	-	-	33.5	-	-	-	-
140-145	2.69	5.60	1570	72	18.4	42.2	12.3	24	51.1	-	100	5.73	37.4	47.4	-	-	-
160-165	2.04	5.58	2160	63	10.2	34.8	-	-	45.6	0.3	-	-	37.6	47.3	-	-	-
175-180	2.01	-	920	68	11.4	27.4	-	-	40.1	-	71	4.27	-	46.7	41.6	11.5	46.9
180-185	2.18	4.84	1040	66	15.9	29.1	6.5	-	35.9	-	-	-	50.8	46.3	-	-	-
Mean (std. dev.)	2.71 (±0.45)	5.93 (±0.73)	2450 (±1840)	78 (±14)	16.3 (±2.8)	46.7 (±11.1)	21.2 (±13.2)	45 (±15)	54.6 (±13.3)	0.3 (±0.1)	98 (±19)	5.57 (±0.76)	36.1 (±6.4)	47.9 (±1.7)			
Range	3.26 to 2.01	7.05 to 4.84	7800 to 920	101 to 63	19.3 to 11.4	61.8 to 27.4	49.0 to 6.5	72 to 24	78.5 to 35.9	0.4 to 0.2	118 to 82	6.49 to 4.27	50.8 to 26.0	51.1 to 46.2			

APPENDIX F. Grain size distribution for Mississippi Delta and Gulf of Mexico Sediments.

Station	Sediment depth (cm)	$CaCO_3$ (%)	SAND >62.5μm	SILT 62.5 to 16μm	SILT 16 to 8μm	SILT 8 to 4μm	SILT 4 to 2μm	CLAY 2 to 0.5μm	CLAY <0.5 m	TOTALS SAND	TOTALS SILT	TOTALS CLAY
Head of Passes (May-June, 1974)	suspended matter	<0.5	<0.2	13.3	14.8	11.8	9.9	22.1	27.9	0.2	49.8	50.0
SW Pass (May-June, 1974)	suspended matter	<0.5	<0.1	8.7	14.8	14.0	5.2	33.1	24.3	<0.1	42.7	57.4
Head of Passes (July 1975)	suspended matter	0.8	<0.1	3.3	10.5	9.0	9.2	33.4	34.5	<0.1	32.0	67.9
SW Pass	sediment		36.5	30.1	6.1	3.8	1.8	7.4	14.3	36.5	41.8	21.7
17	0-5	0.7	35.7	37.8	5.4	3.6	1.7	6.0	9.8	35.7	48.5	15.8
	60-65	0.6	31.5	25.0	7.8	7.5	3.8	8.7	15.7	31.5	44.1	24.4
	110-115	1.2	25.1	33.4	7.5	5.2	4.3	9.0	15.6	25.1	50.4	24.5
12	0-1	0.6	0.2	16.1	9.4	8.8	9.2	20.8	35.4	0.2	43.5	56.2
	0-5	0.7	0.2	18.7	11.1	9.6	9.8	18.7	31.9	0.2	49.2	50.6
	90-95	0.4	<0.1	16.2	11.6	8.8	9.9	19.3	34.2	<0.1	46.5	53.5
	160-165	0.7	7.6	15.0	11.2	8.6	9.2	17.8	30.7	7.6	44.0	48.5
11B	0-1	1.1	0.1	6.1	6.5	10.3	12.5	25.6	38.8	0.1	35.4	64.4
	20-25	0.9	0.1	5.5	14.7	10.7	10.9	23.9	34.2	0.1	41.8	58.1
	50-55	1.1	0.3	11.8	9.3	10.2	9.7	22.4	36.3	0.3	41.0	58.7
	90-95	1.9	0.8	14.6	11.0	8.3	9.7	21.2	34.4	0.8	43.6	55.6
	0-1	3.4	0.2	3.6	4.1	9.7	15.1	24.3	43.0	0.2	32.5	67.3
	0-5	3.0	0.3	4.1	7.0	5.6	12.5	28.2	42.4	0.3	29.2	70.6
	50-55	1.8	0.3	6.0	7.6	9.6	10.8	26.6	39.1	0.3	34.0	65.7
	120-125	1.9	0.7	11.7	9.6	10.0	10.0	23.9	36.1	0.7	41.3	58.0

APPENDIX F (continued).

Station	Sediment depth (cm)	$CaCO_3$ (%)	SAND >62.5µm	SILT 62.5 to 16µm	SILT 16 to 8µm	SILT 8 to 4µm	SILT 4 to 2µm	CLAY 2 to 0.5µm	CLAY <0.5µm	TOTALS SAND	TOTALS SILT	TOTALS CLAY
24	0-5	16.2	2.5	4.0	7.3	11.9	12.7	29.2	32.4	2.5	35.9	61.6
	"	*	<0.1	1.5	6.0	4.6	9.9	26.0	52.0	<0.1	22.0	78.0
	60-65	13.1	3.1	2.8	5.4	10.0	11.5	26.5	39.7	3.1	29.7	67.2
	"	*	<0.1	1.8	6.2	9.2	9.9	24.1	48.7	<0.1	27.1	72.8
	130-135	17.2	2.7	2.2	3.6	7.2	12.3	30.7	41.4	2.7	25.3	72.1
	"	*	<0.1	1.2	1.8	8.8	8.9	28.9	50.3	<0.1	20.7	79.2
4	0-5	*	0.2	6.5	10.9	6.0	11.3	24.7	40.4	0.2	34.7	65.1
	10-15	19.4	10.2	7.2	9.5	8.1	6.2	17.2	41.6	10.2	31.0	58.8
	"	*	<0.1	3.8	11.5	8.1	9.7	21.3	45.6	<0.1	33.1	66.9
	60-65	4.4	0.3	12.5	5.0	5.4	6.6	21.1	49.1	0.3	29.5	70.2
	"	*	<0.1	0.3	4.0	6.3	8.4	26.5	54.5	<0.1	19.0	81.0
	115-120	3.0	0.1	4.3	3.8	7.4	10.2	20.5	53.7	0.1	25.7	74.2
	"	*	<0.1	3.3	5.1	5.8	11.6	23.6	50.6	<0.1	25.8	74.2
5	0-5	36.0	21.2	5.9	5.4	7.0	7.8	34.1	18.6	21.2	26.1	52.7
	"	*	<0.1	5.4	5.3	8.4	8.2	26.5	46.1	<0.1	27.3	72.6
	80-85	8.5	0.7	0.5	5.3	6.3	3.4	30.6	53.2	0.7	15.5	83.8
	"	*	<0.1	1.6	3.3	6.3	5.6	25.4	59.8	<0.1	14.8	85.2
	135-140	8.5	0.5	1.1	2.3	9.5	9.4	23.8	53.4	0.5	21.3	77.2
	"	*	0.1	1.6	1.5	6.2	9.7	25.9	54.8	0.1	19.0	80.7
6	0-5	*	0.2	0.4	1.4	5.9	8.7	31.4	52.0	0.2	16.4	83.4
	5-10	40.3	30.7	15.7	1.8	2.3	10.0	25.6	13.9	30.7	29.8	39.5
	"	*	<0.1	0.7	1.5	2.9	7.5	26.3	56.1	<0.1	17.6	82.4
	100-105	*	0.1	1.7	3.5	5.1	10.7	37.6	42.1	0.1	20.2	79.7
	175-180	50	41.6	0.7	2.9	4.1	3.8	12.5	34.4	41.6	11.5	46.9
	"	*	0.2	3.3	2.6	5.3	13.6	29.1	45.9	0.2	24.8	75.0

VITA

John Harold Trefry III was born to John Harold Trefry, Jr. and Phyllis Nelson Trefry on September 2, 1947 in Boston, Massachusetts. He attended public schools in Quincy, Massachusetts and graduated from North Quincy High School in June, 1965. He enrolled at Syracuse University in September, 1965 and received a Bachelor of Arts degree in Zoology in June, 1969.

Following graduation John accepted a position at Attleboro High School, Attleboro, Massachusetts where he taught Chemistry for three years. In September, 1972 he entered the Graduate College of Texas A&M University and received a Master of Science degree in Oceanography in May, 1974. During his graduate study at Texas A&M he served as a Research and Teaching Assistant in the Department of Oceanography. Since May, 1976 he has worked as a Research Associate in Chemical Oceanography.

John is a member of the American Chemical Society and the Phi Kappa Phi Honor Society. He has published technical papers on trace metal distribution and behavior in marine sediments and riverine and coastal marine water and particulates.

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The typist for this dissertation was Mrs. Lucinda Miller Brooks.